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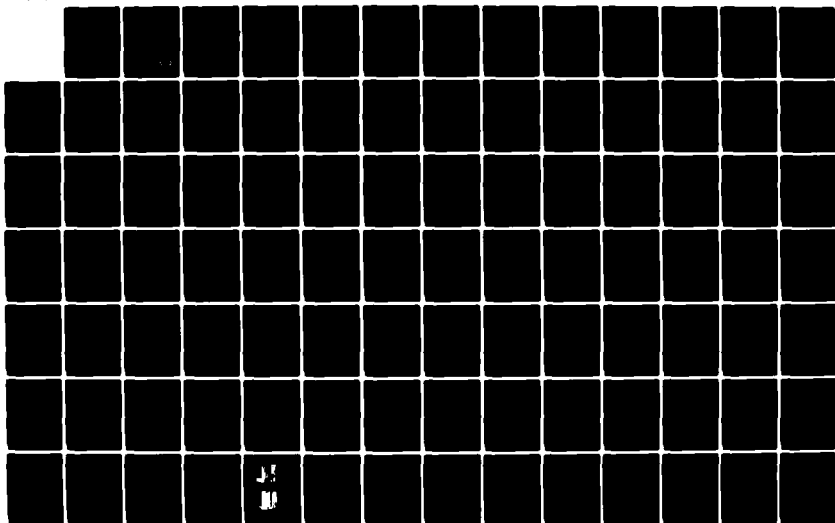
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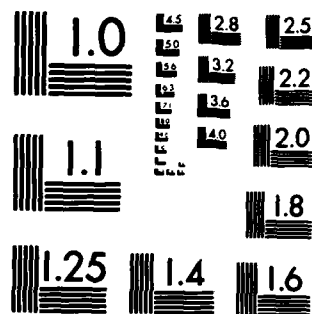
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This Progress Report covers the activities during the first six months of the twelve month project.

The purpose of the investigation reported here was to test four inorganic cementing materials, and screen out from further investigation those that are obviously unsuitable for the fulfillment of the requirements for emergency repair of concrete runways under war conditions. The four materials are, as follows:

SET-45 cold formula

SET-45 hot formula

Aluminum phosphate (A&P) cement

Jet cement.

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In addition, a 50/50 blend of the SET-45 cold and hot formulas was investigated, and a portland cement of Type III was tested for the sake of comparison.

The SET-45 formulas and the AlP cement are based on magnesium oxide. The Jet cement is a modified portland cement.

A combination of mechanical testing and physicochemical examinations was used. The mechanical testing concentrated on the early strength developing capabilities of the cements under room temperature. On this basis the cements of magnesium oxide content, that is the SET-45 formulas appear to be the most suitable for the project. For instance, the SET-45 cold formula can produce compressive strengths in excess of 10,000 psi at the age of 1 hour with low water contents. Even with high water content, enough to produce flowing consistency, the 1-hr strengths are regularly over 3,000 psi. The corresponding setting time of this formula, however, is usually less than 10 minutes even at room temperature. The setting time of SET-45 hot formula is much longer, however its one-hour strength is also reduced. The blend of the two formulas displays in-between strengths and times of setting.

The physicochemical examinations included X-ray diffraction tests, optical and scanning electron microscopy, and infrared spectroscopy. They revealed that the reactions between the SET-45 cements and water produce two different hydration products, one is a monohydrate, the other is a hexahydrate. It appears that monohydrate is associated with the more rapid strength development.

During the remaining six month period the research will concentrate on a more detailed investigation of the mechanical and physicochemical properties of the SET-45 formulas.

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PREFACE

This document is a Progress Report on the project entitled "Materials for Emergency Repair of Runways". The project identified as No. 83-NA-144 by the Air Force Office of Scientific Research (AFSC) is sponsored by the same Office. It started on October 1, 1983, and scheduled to end on September 30, 1984.

The project made use of staff and facilities of the College of Engineering, Drexel University, Philadelphia, PA, 19104. The principal investigator is Dr. Sandor Popovics. Dr. M. Penko has performed the physico-chemical tests as Research Associate and Mr. N. Rajendran has performed the mechanical tests as Research Assistant.

Several companies contributed materials for the project. These include the Master Builders, DuPont Company, and Onoda Cement Company.

EXECUTIVE SUMMARY

MATERIALS FOR EMERGENCY REPAIR OF RUNWAYS

Prepared By: Sandor Popovics
Department of Civil Engineering
Drexel University
Philadelphia, PA 19104

Scope

The primary objective of this project is to find or develop an inorganic cementing material that is suitable for emergency repair of damaged airport runways under war conditions. Although practicality required the use of commercially available cementing materials, considerable new research was needed for this project for two reasons. First, not only are the rapid hardening materials new with little practical or scientific experience to rely on but also they are to be used for a special, new purpose, namely emergency repair possibly with a novel construction technique. Also, attempts have been planned to improve, if necessary, the properties of the commercially available material with modifications.

Therefore, the investigation has been performed in two directions: (a) production of information about the basic nature of rapid hardening cements with or without chemical modifications by using physicochemical methods, such as X-ray diffraction, scanning electron microscopy, infrared spectroscopy, etc.; and (b) performance of laboratory mechanical experiments to determine the technically important properties of these cements.

The project is obviously U.S. Air Force oriented, nevertheless it has important applications in civilian structures. Examples for this are the uses of the obtained results, or their extensions, for repair of concrete structures and potholes in highway pavements, or for overlay on deteriorating bridge decks.

This Progress Report covers the activities during the first half of the project during the period of October 1, 1983 through March 31, 1984.

Method of Procedure

The purpose of the investigation reported here was to test four inorganic cementing materials, and screen out from further investigation those that are obviously unsuitable for the fulfillment of the requirements for emergency repair of concrete runways under war conditions. The four materials were, as follows:

SET-45 cold weather formula

SET-45 hot weather formula

Aluminum phosphate mixture

Jet cement.

In addition two modified versions of the SET-45 cold formula were investigated, and a portland cement of Type III was tested for the sake of comparison.

A combination of mechanical testing and physicochemical examinations was used. All the tests reported here were performed at normal (70 - 75°F) ambient temperature. The effects of higher or lower temperatures will be investigated during the second half of the project.

Description of the Materials

The SET-45 mixtures (Masterbuilders) come in two formulas to cover all weather conditions. One is the "cold" formula which is recommended for cold and regular weather temperatures; the other is the "hot" formula for hot weather conditions. Both formulas are granular materials consisting of a powdery cementitious material and sand in the proportion of 1:4 by weight. The cementitious material is a blend of magnesium oxide (MgO) and ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) with a small amount of flyash. These react with water rapidly producing strength and heat. The hot weather formula also contains boric acid as a set retarder.

The aluminum phosphate (AlP) mixture (DuPont) consists of a granular solid and a liquid component. The solid material is a blend of the powder of magnesium oxide (MgO) with fly ash, sand, and pea gravel in the proportion of 1:1.4:4.1 by weight. The liquid component is a 50% by weight water solution of $\text{Al}(\text{H}_2\text{PO}_4)_3$. The magnesium

oxide reacts chemically with the liquid component producing rapid strength and heat developments.

The Jet cement (Onoda, Japan) is a "regulated set" cement, which is a chemically modified portland cement.

Mechanical Testing

The mechanical testing concentrated on the early strength developing capabilities as well as on the flow and setting times of the cements at room temperature. In one series 27 mixtures were prepared with nine strength specimens from each. In another series 22 mixtures were prepared with 21 strength specimens from each. The compositions are presented in Tables 1 through 7, the flow, setting time and compressive strength results in Tables 8 through 16 as well as in Figures 3 through 19. The following conclusions can be drawn from the results:

1. Workable or even flowing mixtures can be produced with all tested formulas. Traditional plasticizers, including superplasticizers, are not affective with the SET-45 and A&P mixtures.

2. The setting times of the investigated mixtures are typically much shorter than the usual setting times of standard portland cements even when the consistency of the fresh mixture is flowing. The setting times can be extended by admixtures, such as boric acid or borax, but only at the expense of the early strength development. (Figs. 4 and 5)

Considering the shortness of the setting times of the mortars that have high enough 1-hour strength, it is obvious that a special, simple but rapid construction method is needed when these materials, especially SET-45 cold mortars, are used at normal and elevated temperatures. One such possibility is to use a mortar in flowing consistency. Not only would this lengthen the setting time but also it would speed up the construction by the elimination of the need for compaction. This is the reason that the laboratory work presented here has focused on mortars of flowing consistency.

3. The SET-45 cold weather formula develops compressive strengths in excess of 10,000 psi at the age of 1-hour with 5.5% of water content, that is with stiff consistency. Even with 10% water content, enough to produce flowing consistency, the 1-hour strength is over 5000 psi. The 1-hour strengths of the SET-45 hot weather formula, the A&P cements as well as the Jet cement are low. The modified SET-45 cold weather formulas, that is either the cold weather-hot weather formula combination, or the cold weather formula with borax addition, provided 2500 to 3000 psi 1-hour strengths.

At the age of 3 hours the SET-45 cold mixtures gave again the highest strengths ranging from approximately 7000 to 11,000 psi depending on the water content. Its modifications produced 3-hour strengths in excess of 5000 psi. The other materials, namely SET-45 hot, A&P and Jet cements gave strengths between 1500 and 3000 psi.

All mixtures increased their strengths from the age of 3-hours to 24-hours surpassing 10,000 psi strength in several cases with the SET-45 mortars, 5000 to 7000 psi with A&P mortars and 2000 to 4000 psi with the Jet cement. The most dramatic increase was observed with the SET-45 hot mortars. (Figs. 9 through 14)

Further strength increases were observed with SET-45 mortars up to the age of 90 days. An exception is SET-45 cold mortars which show regularly a strength retrogression from the 7-day strength to the 28-day strength after wet curing. (Tables 16 and 17 as well as Figs. 15 and 16.) This strength reduction is attributed to the cracking of the strength specimen (Fig. 20) which is the consequence of recrystallization of hydration products discussed later on. This also means that wet curing is not only unnecessary for SET-45 mortars but also that it can be harmful.

The two SET-45 cold mortars with superplasticizer and with epoxy, respectively, produce low strengths indicating chemical or physical incompatibility (Table 11).

Physicochemical Investigations

The physicochemical investigations have also produced several new and important results. Optical microscopy provided a useful picture of the compositions of the

materials under investigation in their dry granular state. Scanning electron microscopy provided details about the internal structure and morphology of the hydration products (Figs. 72-80), and X-ray diffraction and infrared spectroscopy gave information about the compositions of the hardened cement pastes. The analysis of these test results revealed, for instance, that the hydration products of the SET-45 mixtures are mainly ammonium magnesium phosphate hydrates.

Even more interesting is the revelation that the phosphate hydrate can occur in the hydration products both as a monohydrate ($\text{NH}_4\text{MgPO}_4 \cdot \text{H}_2\text{O}$), and as a hexahydrate ($\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$). (Fig. 43) The monohydrate-hexahydrate ratio can vary within wide limits depending on the prevailing circumstances. It has been established, for instance, that cold weather formula and/or low water content increases the mono-hexa ratio in the hydration product.

Probably the most important discovery has been, however, that the monohydrate may convert into hexahydrate by recrystallization if enough water is available. For instance, the X-ray diffraction of a SET-45 hot weather paste with 0.375 water-cement ratio by weight showed monohydrate present along with hexahydrate at the age of 3 days (Fig. 32) but at the age of 7 days the peak of the monohydrate disappeared from the X-ray diffraction showing only the presence of the hexahydrate (Fig. 33). Since the hexahydrate has a larger volume than the monohydrate, the recrystallization causes a volume increase which, in turn, causes expansion and eventually cracking of the hardened mortar. This mechanism is offered as a possible explanation of the cracking of the SET-45 cold mortar specimens (Fig. 20) and the observed strength reductions of these mortars at the age of 28 days.

Comparison of the Materials

Based on the test results obtained up to this point of testing, the advantages and disadvantages of each material under investigation can be summarized, as follows:

1. The same water content under identical conditions produces the lowest viscosity in SET-45 hot formula, and the highest viscosity in the A&P mixtures. (Tables 1 and 6)

2. SET-45 cold formula has the shortest setting times (initial set is less than 10 minutes, final set is less than 15 minutes at room temperature), and SET-45 hot formulas has the longest ones. (Figs. 4 and 5)

3. The highest compressive strengths at the ages of 1 and 3 hours are developed by SET-45 cold weather mortar. The measured 1-hour strength, for instance, was more than 5000 psi with 10% water (flowing consistency) at room temperature which is perhaps unnecessarily high strength for the given purpose. (Fig. 9) On the other hand, its setting times are the shortest, initial setting being less than 10 minutes at room temperature and probably much less at elevated temperatures. Also this is the material that has the tendency to convert the monohydrate to hexahydrate with the potentiality of causing cracking in a week or so in the hardened mortar. Finally, this material develops the most heat within a few hours.

4. The SET-45 hot weather mortar has much longer setting times and develops less heat due to the presence of boric acid. However, it produces little strength at room temperature during the first 3 hours. It is very likely that at elevated temperatures the early strengths as well as setting and heat development will be similar to those of the cold weather formula at room temperature.

5. The modified SET-45 cold weather mortars, that is, the 50-50 blend of cold weather-hot weather formulas, as well as the cold weather formula with borax addition, seem to combine the advantages of the two individual formulas.

6. The A&P mortars and the Jet cement mortars can reach compressive strengths between 1500 and 3000 psi at the age of 3 hours despite the fact that their 1-hour strengths are quite low. The setting times are similar to those of the modified SET-45 cold weather mortars. (Tables 12 through 14)

Future Work

The work during the concluding six months of the project will concentrate on the indepth investigation of various SET-45 formulas but the A&P mixture will also be tested to a certain extent.

All mortars will have fluid consistency. Combinations of mechanical and physico-chemical tests will be used again.

Among others, the testing of the following mechanical properties is planned:

Compressive and flexural strengths at room temperature up to 90 days

Setting times and early compressive strengths with specimens made with heated and unheated mixing water, and cured at a temperature around freezing point

Setting times and early compressive strengths with specimens made with cooled and uncooled mixing water, and cured at 100°F

Shrinkage

Bond to old portland cement concrete.

In the physicochemical investigations again optical and electron microscopy, X-ray diffraction, and infrared spectroscopy will be used. The investigation will concentrate on the modification and optimization of the SET-45 formulas. Among others, the following items will be investigated:

Hydration and hydration products of the different formulas

Recrystallization process of the monohydrate and its reduction

Increase of time of setting at high temperatures without hurting the early strengths too much

Increase of early strengths at low temperatures by admixtures.

A preparation of the Final Report will conclude the project.

Conclusions

It is not a problem to produce compressive strengths in excess of 2000 psi after 1-hour at room temperature. After all the SET-45 cold weather formula has approximately 5000 psi strength even with flowing consistency. The problem is the shortness of the time of setting of this formula. This problem is even more severe at elevated temperatures.

Fortunately the 1-hour strength of the cold formula is so high that it leaves place for compromises in several directions based on further research. This way it

may be possible to increase the time of setting by a suitable admixture, or by a higher water content, or by a higher sand content, or by a combination of these, and still achieve the needed 2000 psi strength at the age of 1-hour. If further research in these directions remains still unsuccessful, special construction technique should be used. Such a technique is to mix the SET-45 formula as a flowing mixture in a movable mixer and pouring it immediately into the damaged area.

Problems caused by low or high ambient temperature will be faced in the second half of this project.

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1. INTRODUCTION

1.1 General

The primary objective of this project is to find or develop an inorganic cementing material that is suitable for emergency repair of damaged airport runways under war conditions. Although practicality required the use of commercially available cementing materials, considerable new research was needed for this project for two reasons. First, not only are the rapid hardening materials new with little practical or scientific experience to rely on but also they are to be used for a special, new purpose, namely emergency repair possibly with a novel construction technique. Also, attempts have been planned to improve, if necessary, the properties of the commercially available materials with modifications by chemical admixtures.

Therefore, the investigation has been performed in two directions:

(a) production of information about the basic nature of rapid hardening cements with or without chemical modifications by using scientific methods, such as X-ray diffraction, scanning electron microscopy, infrared spectroscopy, etc.; and (b) performance of laboratory mechanical experiments to determine the technically important properties of these cements.

The project is obviously U. S. Air Force oriented, nevertheless it has important applications in civilian structures. Examples for this are the use of the obtained results, or their extensions, for repair of potholes in highway pavements, or for overlay on deteriorating bridge decks.

This Progress Report covers the activities during the first half of the project during the period of October 1, 1983 through March 31, 1984.

1.2 Objectives

The specific objective of the proposed research is to find an inorganic cement with the following properties:

1. Development of at least 2000 psi compressive strength in one hour, even in cold weather.
2. Development of a sufficient flexural strength.
3. At least 10 minutes of time of initial set, even in hot weather.
4. Sufficient workability of the fresh mixture.
5. Sufficient bonding capability of the new mixture to old concrete.
6. Negligible shrinkage to avoid bond failure and cracking.
7. Sufficiently high and permanent final strength.
8. Reasonable cost of the finished repair.

1.3 Scheduling

In the first half of the 12-month project the technical literature was searched and reviewed. On this basis four promising cementing materials were selected; these were submitted to a series of scientific and engineering screening tests to establish which cement is the most promising for the specified emergency repair.

The coming second half of the project will concentrate on the in-depth investigation of the properties and applicability of the selected cement(s). Modifications will also be tried out to optimize the cement for the primary objective of the project.

2. PRELIMINARY WORK

2.1 Review of Literature

The review of pertinent literature revealed that two kinds of cements might develop strength very rapidly. One kind is the magnesia-based cements, the other is the regulated set (portland) cements. High-alumina cements, mixtures of high-alumina and portland cements as well as portland cements with accelerators were judged inadequate for this project.

2.2 Selection of Cements

On the basis of the review of literature, the following cements were selected for a preliminary investigation:

SET-45 cold formula

SET-45 hot formula

Aluminum phosphate mixture

Jet cement

Type III portland cement.

In addition, sand, crushed stone and several admixtures were used in the experiments. All these materials are described in Section 3.

3. DESCRIPTION OF THE MATERIALS

3.1 SET-45 Mixtures

These mixtures come in two formulas in order to cover all weather conditions. One is the "cold" formula and recommended for regular and low temperatures. The second is the "hot" formula and is for hot weather conditions. These products are commercially available granular materials delivered in 50 lb paper bags. They are manufactured by Masterbuilders in the plant of SET Products, Inc., Macedonia, Ohio. The product was designed for fast repair of patching potholes. The number "45" implies that the repaired spot is ready for use in 45 minutes after placement. The manufacturers claim that both formulas when properly used, produce strength that exceeds 2000 psi in an hour yet allow enough time for placement.

Both mixtures are light gray, granular materials. The manufacturer does not specify the compositions of the products. Our own findings, discussed in detail later in this report, are that the product is a mixture of a powdery cementitious material and sand in the proportion of 1:4 by weight. The sieve curve of the hot formula is presented in Fig. 1. The grading of the cold formula is practically the same.

The cementitious material is magnesium oxide (MgO) and ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) with a small amount of fly ash. These react with water rapidly producing strength and heat. Also, the hot weather formula contains boric acid (not specified amount) as a retarder.

This report will refer to these two formulas in dry, granular state as "SET-45 cold mixture" and "SET-45 hot mixture." When water is added to a mixture it is called "mortar" instead of mixture. A third term used in this report is "cement." This is the portion of the mixture that passes No. 200 sieve. The mixture of cement and water is called "paste."

3.2 Aluminum Phosphate (ALP) Mixture

This product is still in the stage of development and does not have a trade name yet. The formulation is based on the United States Patent No. 4,394,174 (July 19, 1983) owned by E. I. DuPont De Nemours & Company, Inc., Wilmington, Delaware. It is a two component product, one is liquid and the second is a granular solid. The compositions, as given to us by the inventor, are the following:

The liquid is 50% (by weight) water solution of $\text{Al}(\text{H}_2\text{PO}_4)_3$.

The solid component consists of a powdery cementitious material, sand and pea gravel in the proportion of 1:1.4:4.1 by weight. The sieve curve of the solid components is presented in Fig. 2. The cementitious material is MgO and fly ash. It reacts chemically with the liquid component. The mixing proportion recommended by the manufacturer is 11% (by weight) of liquid with 89% (by weight) of solid.

This report will refer to the dry granular solid phase as "ALP mixture," and to the liquid phase as "ALP solution." Their combinations without pea gravel are called "ALP mortars," and with pea gravel as "ALP concretes." "Cement" or "ALP cement" mean again the solid material passing sieve No. 200. The mixture of cement and liquid is called "paste."

3.3 Onoda Jet Cement

This is a yellowish powdery material with the appearance of portland cement. It is manufactured by Onoda Cement Co., Ltd., Tokyo, and available commercially in Japan. It is a so-called "regulated set cement" without any aggregate, that is, a special modification of portland cement first developed by Portland Cement Association (PCA) Skokie, Illinois. The patent (U. S. Patent No. 3,628,973, December 21, 1971) has been sold to Japan. The composition is reported by its designer in Cement and Concrete Research, Vol. 3, No. 3, 1973, pp. 263-277, where also the hydration and early strength development are discussed. The reported fineness is $5630 \text{ cm}^2/\text{g}$.

According to this article, the main difference between jet cement and traditional portland cement is that in jet cement the C_3A phase is replaced with a calcium haloaluminate having the formulas $11\text{CaO} \cdot 7\text{Al}_2\text{O}_3 \cdot \text{CaX}_2$ ($\text{C}_{11}\text{A}_7\text{CaX}_2$). This latter is even more reactive than C_3A and an addition of a sulfate more soluble than gypsum is needed. Calcium sulfate hemihydrate may be added therefore. Consequently, the main hydration product at early stages is ettringite which is responsible for the high early strength development. This also means that the early strength development can be regulated by controlling the ettringite production with varying the amount of $\text{C}_{11}\text{A}_7\text{CaX}_2$. This cement is referred to in this report as "Jet cement", and the combination with sand and water as "Jet mortar."

3.4 Portland Cement, Type III

A commercially available portland cement of Type III produced by Whitehall Cements was used for comparison purposes.

3.5 Superplasticizers (High-range water-reducing admixtures)

Plastocrete 161R is manufactured by Sika, Inc. It is a non-air entraining admixture complying with the specification for Type D high-range water-reducing admixtures in ASTM C-494.

Pozzolith 200-XR is manufactured by Masterbuilders, Cleveland, Ohio.

Mighty 150 is manufactured by ICI Americas Inc., Wilmington, Delaware.

It conforms to ASTM C494 for Type F and Type A high-range water reducing admixture.

3.6 Other Materials

Nicklepoxy is an epoxy manufactured by Rocky Mountain Chemical Company, Casper, Wyoming, 82602. It contains two components. The component A is called resin and component B is called curing agent. The following blending proportions are recommended by the manufacturer:

Component A (resin) 3.3% by weight

Component B (curing agent) 0.5% - " -

The borax used is manufactured by Fluka Chemical Corp., 255 Oser Avenue, Hauppauge, NY. The chemical name of the component is 'Sodium tetraborate Decahydrate' ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$). Its actual borax content is greater than 99%.

4. MECHANICAL TESTS

4.1 Scope

The mechanical tests, up to this point of time have served as screening tests for the elimination of the materials obviously unsuitable for the fulfillment of the objectives.

This portion of the investigation consisted of testing the early strength developing capability of each of the four cements in concretes of flowing consistency at the ages of 1, 3 and 24 hours after standard curing. Flow and times of setting were also measured.

The compositions of the tested mortars and concretes are presented in Tables 1 through 7.

4.2 Preparation of the Specimens. Tests on Fresh Concrete

Mixing

The mixer was a three-speed bench model of approximately 1/6 cu. ft. capacity with a stainless steel bowl and planetary action. It complies with ASTM C305.

The mixing procedure used for all batches is, as follows:

The mixing water was poured into the bowl. The dry components were premixed and added to the water. These were mixed together first for 30 s at low speed, then for 90 s at medium speed.

When an admixture was used, it was premixed with the mixing water, or with a portion of it.

Flow and Time of Setting Tests

Immediately after mixing the flow test and time of setting test were performed in accordance with ASTM C 230-80 and C 191-77, respectively.

The pertinent test results are presented in Tables 8 through 14. The water content is expressed as percent by weight of the dry mixture.

4.3 Experiments with Plasticizers

Plasticizers, or water-reducing admixtures, are chemicals that, when added to the fresh concrete in the mixer in a very small quantity, improve the fluidity of the fresh concrete without any major harmful side effect. A wide variety of plasticizers have been used with portland cement concrete for a long time but no experiments have been found in the literature about their use with very rapid hardening cements. Therefore it was decided to try out some of the plasticizers recommended for portland cements with the four cements included in our investigation. These plasticizers are, as follows:

Mighty 150	}	Superplasticizers
Melment		
Plastocrete 161R		
Plastocrete 161		
Pozzolith 100R	}	Plasticizers
Pozzolith 100XR		
Pozzolith 122R		
Pozzolith 122N		
Pozzolith 122HE		
Pozzolith 200XR		

These plasticizers have been tried out with the following cements and mixtures:

SET-45 cold mixture
 SET-45 cold cement
 SET-45 hot mixture
 SET-45 hot cement
 A&P mixture
 A&P cement
 Jet Cement
 Portland Cement Type III
 Portland Cement Type III Mortar

For testing purposes the plasticizer was added to the mixing water in the quantity recommended by the manufacturer. Then a paste or mortar was prepared with this liquid.

The effects of plasticizers on the fluidity were observed visually. It was established that none of the tested plasticizers was effective with the SET-45 cements or with the A&P cement. They were effective, however, with the Jet cement, and, of course, with the portland cement. Especially the superplasticizers worked well. It was also noticed that the plastification was less when the plasticizers were used in mortar made with the Jet and portland cements.

Further chemicals that may be suitable for plastification of rapid-hardening mortars and concretes are the following:

Organosilicons appear promising with magnezium-based cements.

Polyelectrolites are salts of polymeric acids. After dissociation the anions become long and have negative electric charges. If they are adsorbed on the surface of solid particles they create repulsive forces between the particles. This should lower the viscosity, that is, increase the fluidity.

Inorganic salts. Phosphate cements seem to be sensitive to the water media. With changing the concentration of different ions in cement suspension or with an addition of new cations that form complexes with phosphate anions, there is a hope to influence the viscosity. These chemicals will be tried out in the near future.

4.4 Strength Tests

In one series 27 mixes with nine 2-in cubes were prepared for each mix essentially in accordance with ASTM C 109. The cube specimens were removed from the mold after 45 to 50 minutes and air cured under room temperature at $73.4^{\circ}\text{F} \pm 3^{\circ}\text{F}$ until the break.

The compression tests on cubes were carried out in accordance with ASTM C 109. Tests were run on specimens at the age of 1 hour, 3 hours, and 24 hours. Three specimens were tested for each specific age. The strength at room temperature are given in Tables 8 through 14.

In another series, 22 mixes with 21 2-in x 4-in cylinders each were cast in metal molds essentially in accordance with ASTM C 192. They were stripped in 45 to 50 minutes and kept at room temperature ($73.4^{\circ}\text{F} \pm 3^{\circ}\text{F}$) for 24 hours. Then they were kept also at 73°F in a moist room until the break. The moist room complies with the specifications in ASTM C 511-78.

For compression tests the ends of the cylinders were capped in accordance with ASTM C 617 76. Tests were run on specimens aged 1 hr, 3 hrs, 24 hrs,

1 day, 7 days, 28 days, and 90 days. Three specimens were tested for each specific mix. The strengths at room temperature are presented in Tables 15 and 16.

5. ANALYSIS AND DISCUSSION OF MECHANICAL TEST RESULTS

5.1 Flow

The relationship between flow and water content for SET-45 cold and hot mortars is shown in Figure 3. It can be seen that the flow increases with an increase in water content as expected but the rate decreases at higher water contents for both mortars.

The figure also shows that SET-45 hot mortars produce larger flow than SET-45 cold mortars under identical conditions. This is attributed to the presence of boric acid in the hot mixture. Similar trend was observed when a small quantity of borax was added to the cold mixture. Consequently, it is not surprising that the flows for the cold mixture blended with hot mixture, and cold mixture blended with borax are between the flow of cold mortar and that of the hot mortar. (Tables 8 through 10)

The data from Tables 12 through 14 also show that the ALP and Jet mortars exhibit less flow at the same water content than the comparable SET-45 mortars. Further, it was observed during mixing that the ALP mortars are stickier than other mortars. It can also be seen from Table 13 that the 100 percent flow was achieved only once by using 18 percent liquid in ALP mixture.

Efforts were made to improve the fluidity of mortars by the use of plasticizers and superplasticizers. The obtained test results show, however, that these admixtures worked well only with the Jet cement and portland cement (Table 14).

5.2 Setting Time

The initial and final setting times for SET-45 mortars are shown in Figures 4 and 5. It can be seen that the initial setting times of the SET-45 cold formula is regularly less than 10 minutes, and the time of final setting is less than 15 minutes at room temperature. These settings times are too short for the traditional construction techniques therefore the manufacturer came out with another formula, the SET-45 hot mixture which has much longer times of setting. It can also be seen that the fifty-fifty blend of cold and hot formulas as well as cold formula with borax have in-between setting times. The delay in settings in the latter formulas is due to the presence of boric acid that acts as a retarder.

Another noticeable trend is that the setting times decrease with decreasing water content more or less in the same way as the setting time of portland cement. The time of setting of the A2P concretes and A2P mortars are between those of comparable SET-45 cold and SET-45 hot mortars. The same statement is valid for mortars made with Jet cement except for mixture JWB7 where a plasticizing admixture was used. Here the times of setting are very long but, unfortunately, the strengths are also low.

During the setting process cements develop heat since the hydration is an exothermic process. The faster the setting, the faster the heat development. Thus the SET-45 cold formula is the one that develops the heat of hydration most rapidly and in the largest quantity. The heat development can be reduced by any method that extends the times of setting.

Considering the shortness of setting times of the mortars that have high enough 1-hour strength, it is obvious that a special, simple but rapid construction method is needed when SET-45 mortars are used. One such method is where the mortar is used in a fluid state instead of the usual plastic consistency. Not only would this lengthen somewhat the setting time but

also it would speed up the construction by the elimination of the need for compaction. For this reason the work presented here has focused on mortars of fluid consistency.

5.3 Compressive Strength

Compressive Strength Versus Water Content

Compressive strength versus water content for SET-45 mortars at 1, 3, and 24 hours are shown in Figures 6 through 8. It can be seen from the figures that, for all cases, the SET-45 cold mortar exhibits higher strengths than the other SET-45 mortars up to the first 24 hours. Further, high early strength of about 10,000 psi was achieved within an hour with low water content. The general trend is that the strength of SET-45 cold mortar decreases with an increase in water content, except the strength at medium water content (8%) at 24 hours. Similar trend was observed with SET-45 hot mortars. However, in almost all cases, the SET-45 hot mortar exhibits less strength than the other SET-45 mortars.

Borax blended with SET-45 cold, and SET-45 hot blended with SET-45 cold formula, exhibit different behavior, that is, the strength is more at high and low water contents than at medium water content at the age of 1 and 3 hours, but at the age of 24 hours the strength decreases with an increase in water content. The reason for these discrepancies is not clear at present.

Compressive Strength Versus Age

In general, the minimum requirement of 2000 psi strength within an hour was achieved for all water contents with SET-45 cold mortar with SET-45 cold formula with borax addition, and SET-45 cold with hot formulas except for the strength at medium water content for SET-45 cold with borax, and SET-45 combination of cold with hot formula.

In the case of SET-45 hot mortar, the early strength of 2000 psi at an hour was not achieved. As a matter of fact, the mortars were so weak that the specimens broke during their removal from the mold.

The relationships between cube strength and early age (up to 24 hours) of SET-45, A1P, and Jet mortars are presented in Figures 9 through 14. It is apparent that the strength increases with an increase in age for all mortars similarly to conventional portland cements although the rate of strength development is greater. For almost all cases, the strength of SET-45 cold mortar exhibits higher early strength than the other mortars. It can be seen from Figures 9 through 11 that there is sudden increase in strength for SET-45 cold mortar up to the age of 3 hours after which there is not much appreciable rise in strength. In contradistinction, the strength of SET-45 hot mortar starts increasing rapidly after the age of 3 hours.

In general, SET-45 hot mortars exhibit less strength compared to SET-45 cold mortar at room temperature.

It is quite apparent that the strength of the blend of SET-45 cold with SET-45 hot formula falls between these two mortar strengths as expected. Similar phenomenon was also observed when a small quantity of borax was mixed with hot mortar.

Further, it can be seen from Figures 12 through 14 that the A1P concrete and mortar and also Jet mortar produce less than 2000 psi strength at the age of one hour which is a basic requirement. The strengths start gaining only after 3 hours. However, these strengths are less than the SET-45 mortars with comparable water contents.

The relationship between cylinder strength and age of SET-45 mortars up to 90 days are shown in Figures 15 through 18. It can be seen that the strengths of SET-45 cold mortars increase up to 7 days, then there is a decreasing strength reduction at the age of 28 days, after which they start

increasing again. It was also noticed that the specimens made with more than 8% water content cracked. These cracks started approximately at the age of 3 to 4 days in the fog room. It is believed that the cracking is due to the moist curing. An example for the cracked specimens are shown in Figure 20. The source of the new gain in strength after 28 days is not clear at present.

No strength reduction was observed with SET-45 hot mortars. (Figures 17 through 18.)

Cylinder Strength Versus Cube Strength

The relationships between cube strength and cylinder strength of SET-45 hot mortars with various water contents are shown in Figure 19. It can be seen that this relationship is a function of the mortar type and age. Since these factors have no significant role in the case of portland cement mortar specimens, one may attribute this effect to the rapid heat development of the SET-45 mortars. Note also that at low water content, the cylinder strength is greater than the cube strength at the age of 3 hours.

6. PHYSICOCHEMICAL EXAMINATIONS

6.1 Scope

Parallel to the mechanical tests, physicochemical examinations were also performed. The purpose of these tests was to obtain an understanding of the basic nature of the rapid hardening materials under investigation; and subsequently, to find ways to improve one or more of them for the specific purpose of the project.

The following tests were performed for the study of composition, morphology and hydration process:

Optical microscopic examination of materials under investigation

Hydration monitored with optical microscope

pH measurements

X-ray diffraction examination

Scanning electron microscopy (SEM)

Infrared spectroscopy (IR).

Special attention was paid to the SET-45 mixtures because they appear to be the most promising for the project.

6.2 Optical Microscopic Examinations

Three out of four products under investigation are manufactured as mixtures of a cementitious material, sand, fly ash and possibly some other additives. Only the fine size fractions of these mixtures were examined with optical microscope.

The equipment used was an optical microscope manufactured by Bausch and Lomb, Inc. A magnification of 45 was applied regularly.

The observations are presented below.

SET-45 Cold Mixture

Fraction #16 - #30: Most of the material retained resembles quartz. In addition, there are a few white chunks observed that dissolve in diluted HCl with fizz. This could indicate a small quantity of carbonates present.

Fraction #30 - #50: Again most of the material is quartz. The number of white chunks increases. They also dissolve with fizz in diluted HCl. In addition, some black irregularly shaped particles are found that float on water and seem to have organic origins. They might be coal particles.

Fraction #50 - #100: Quartz and some carbonate are present on sieve no. 60. The number of black particles increases. In addition, white spheres are detected - very probably fly ash. They do not react with diluted HCl. Quartz crystals are covered with tiny solute crystalline material that seems to dissolve in diluted HCl. These particles are too small to observe any fizzing. They could be carbonate or oxide. Since we know that magnesium oxide is one of the active components in the mixture,

we think that the tiny particles are MgO.

Fraction #100 - #200: The amount of the black particles is larger. An even larger (~50%) amount of white spheres is observed.

Fraction passing sieve #200: Black particles are still present but in a smaller amount. The rest is a seemingly homogeneous new phase not observed on the earlier sieves. When diluted HCl is added, part of this material dissolves and clusters of needlelike crystals are formed. Due to the complexity of the system, one cannot tell what these crystals are without additional experiments.

SET-45 Hot Mixture

All the features described at SET-45 cold mixture are true also for SET-34 hot mixture but, in addition to the already described particles, new particles are also observed. Their concentration is the largest in the #30 - #50 and #50 - #100 size fractions. Still, the number of these particles is small compared to the number of other particles. The new particles are white, irregular in shape and they dissolve in water relatively slowly. Knowing from our experiments that borax is a retarder for SET-45 mixtures, we thought that perhaps borax was added to SET-45 (hot) mixture at the plant. We compared these particles to particles of crystalline borax, manufactured by FLUKA company. These borax particles dissolve at a similar slow rate in water as the unknown particles in SET-45 (hot) mixture, but they are better crystallized and therefore have different appearance. The amount of the particles is too small to be detected by X-ray. A hint from the manufacturer of SET-45 is that boric acid is added which presumably has similar retarding effect as borax.

In addition to the above observations, big white chunks are occasionally found in both SET-45 mixtures that are retained even on sieve no. 4. An examination with X-ray diffraction showed them to be ammonium dihydrogen phos-

phate. The problem related to this finding is discussed together with X-ray diffraction examination.

A&P Mixture

Fraction #30 - #50: The material retained is composed of four different phases:

Clear transparent crystals

Brown transparent crystals

Opaque white crystals

Irregular white material.

When a few drops of diluted HCl were added no reaction was visible. This means that no carbonates or oxides are present. The conclusion may be that all the crystals are probably some form of SiO_2 . Most of them probably are quartz with a different degree of purity.

Fraction #50 - #100: The same four types of crystals are present as those retained on sieve No. 50. In addition, two new phases occur, white spheres and black irregular particles. Neither the white spheres nor the black particles react with diluted HCl. The white spheres look the same as those found in SET-45 mixtures and are identified as fly ash. The black particles look also the same as those found in SET-45 mixtures and are identified as organic material, most probably coal.

Fraction #100 - #200: The same materials were observed as on sieve no. 100. The amount of brown crystals is larger.

Fraction passing sieve #200: It consists mainly of small crystals that slowly dissolve, without bubbles, in diluted HCl. They were identified with X-ray diffraction method as magnesium oxide (MgO) particles. Besides, all the particles that were retained on sieve no. 200 can be found also in the pan. The amount of black particles is even larger than on sieve no. 200.

6.3 Hydration Process Monitored with Optical Microscope

Pastes were prepared from the material passing sieve #200 and examined under optical microscope immediately after mixing. The equipment was the same optical microscope (Bausch and Lomb Inc.). The magnification used was 45.

The observations are presented below.

Paste of SET-45 Cements

When water is added to SET-45 cements, clusters of crystals disappear immediately by bursting like a foam on water. The bursting of crystal clusters is a combination of two processes, namely dissolution and sinking. When all particles not dissolved are sunk, the liquid above them is still moving, an indication that there is still some chemical activity present. However in a matter of minutes the liquid gets thicker and finally crystallizes, forming a bond between the undissolved particles consisting very probably of the magnesium oxide phase. No other changes are observed later on, that is, within a few hours.

A basic difference becomes obvious between the SET-45 cold, and SET-45 hot mixtures. The two cements in powder form look the same but when they are mixed with water, the phase that has been hiding the difference gets dissolved (phosphates). The magnesium oxide particles that do not get dissolved during this early time of hydration differ. The size of magnesium oxide particles in SET-45 cold paste is much smaller than the size of magnesium oxide particles in SET-45 hot paste. This difference may contribute to faster hardening of SET-45 cold mortars.

Pastes of A&P Cement

Here, instead of water, A&P solution is added to the cement. No immediate activity was observed. All the particles sank to the bottom. The liquid phase is very viscous and does not crystallize. This is the most important

difference between A&P paste and SET-45 pastes. The liquid does not crystallize even after it hardens. Some solid amorphous product is formed instead. The much higher crystallinity of the SET-45 pastes in these first hours of hydration probably accounts for their much higher early strength.

Jet Cement and Portland Cement Type III

No immediate activity is observed in both systems after mixing it with water. The liquid phase slowly evaporates and when the samples dry, a thin solute layer is formed at the bottom. This is very probably calcium hydroxide.

6.4 pH Measurement

Slurries were prepared with the various mixtures and the value of pH was measured repeatedly. The purpose of these tests was to check the potential compatibility of the examining mixtures with each other.

Digital pH meter "DIGI-SENSE" (Cole-Parmer Instrument Company) was used. It was calibrated with standard solution (pH = 7.0). SET-45 mixtures and A&P mixtures were used as they are, that is in the presence of aggregate. Jet cement and portland cement Type III were mixed with sand in ratio of cement:sand = 1:4 by weight. 11% of water was added with respect to the total weight of cement and sand. This high amount of water was used to make sure that the electrode is in a good contact with the slurry.

The results are presented below.

SET-45 Cold Mortar

SET-45 mortars set fast and develop high temperatures. To protect the electrode the pH was monitored only for short periods of time. The pH that the slurries had before they set is, as follows:

pH = 5.19 T = 26°C - 28°C

SET-45 Hot Mortar

The test was performed in the same way as above.

pH = 4.85

A&P Mortar

A constant increase is observed in this mortar with the time of hydration. The A&P solution alone has pH = 1.34. The hydration process is a neutralization process. The increase of pH here is very probably proportional to the degree of hydration.

<u>Time Elapsed</u>	<u>pH</u>	<u>Temperature, °C</u>
0 minutes	1.34	(liquid only)
2 "	1.44	28
3 "	1.56	28
5 "	1.61	29
10 "	1.89	30
15 "	2.07	31
20 "	2.25	"
25 "	2.46	"

Jet Mortar

<u>Time Elapsed</u>	<u>pH</u>	<u>T = 25°C</u>
6 minutes	12.56	
10 "	12.37	(pH meter was readjusted)
15 "	12.43	
20 "	12.39	
25 "	12.43	
30 "	12.43	

Portland Cement Type III Mortar

<u>Time Elapsed</u>	<u>pH</u>	<u>T = 22°C</u>
10 minutes	12.58	
12 "	12.58	
15 "	12.72	
20 "	12.72	
25 "	12.73	
30 "	12.74	

It follows from the pH determination that SET-45 cold mixture is compatible with SET-45 hot mixture, and that Jet cement mixture is compatible

with portland cement Type III. A2P mixture is not compatible with any of the examined mixtures.

6.5 X-Ray Diffraction

SET-45 Cements and Pastes

SET-45 mixtures, in the form as they are, are not suitable for X-ray diffraction analysis. About 80% of their weight is sand which dilutes the active chemicals. The mixtures were therefore sieved through sieve no. 200 and only the passing material, that is the cement, was examined with X-ray diffraction method.

During sample preparation some white chunks were observed that were thought first to be limestone pieces as described at examination with optical microscope. X-ray examination of a few chunks, however, showed that they are ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) which is an active ingredient in SET-45 mixtures. Nevertheless, the material passing sieve no. 200 still shows the presence of $\text{NH}_4\text{H}_2\text{PO}_4$ meaning that most of the phosphate is in a fine powder form. Another problem was that boric acid present in the SET-45 hot mixture is almost totally sieved out. Most of the boric acid retains on sieves no. 50 and 100. This, however, was fortunate to some extent because it helped us find out that the MgO phases in SET-45 cold and SET-45 hot mixtures are not the same.

The X-ray diffractometer (General Electric) was used with CA-7 diffraction tube. Copper K_α radiation was applied and all the patterns were run at the same settings of the diffractometer.

SET-45 cements (hot and cold weather formulations) yield rather similar X-ray patterns (Figs. 21 and 22). Both are composed for two crystalline ingredients, namely MgO and $\text{NH}_4\text{H}_2\text{PO}_4$. In X-ray pattern of the SET-45 hot cement an additional small peak is observed at $2\theta = 27^\circ$. This peak belongs to quartz. SET-45 hot mixture passing sieve no. 16 was also examined in an

attempt to detect boric acid (Fig. 23). However, this attempt was unsuccessful because its quantity is too small to be detected. In the corresponding X-ray pattern the only new but expected feature was a big increase of the quartz peak at $2\theta = 27^\circ$.

Four different pastes were prepared with two different water-cement ratios, namely at 0.525 and 0.375 by weight. These two ratios correspond to the water to solid ratios of 0.1 and 0.075 when the sand is not sieved out. The cements were the following:

1. SET-45 cold cement
2. SET-45 cold cement + 1.7% borax
3. SET-45 hot cement
4. 50% SET-45 cold cement + 50% SET-45 hot cement.

Mixing was performed in plastic vials that were sealed with a very tight lid and stored at room temperature. X-ray patterns were taken at 1 hour. As far as the hydrated SET-45 pastes are concerned, it was seen from the X-ray patterns that there are no ammonium dihydrogen phosphate peaks present any more after one hour, or even 20 minutes of hydration. Instead, some new peaks show up. This indicates that the $\text{NH}_4\text{H}_2\text{PO}_4$ is dissolved and reacted quickly. This is true for all four examined systems at both water-cement ratios.

The two major products of this early hydration have been identified as ammonium magnesium phosphate hexahydrate ($\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$) and ammonium magnesium phosphate monohydrate ($\text{NH}_4\text{MgPO}_4 \cdot \text{H}_2\text{O}$). We will call them just hexahydrate and monohydrate. Four diffraction peaks are cited for monohydrate in literature, two intensive and two weak. The intensive peaks are $d = 9.00\text{\AA}$ and $d = 28\text{\AA}$. The weak peaks are $d = 4.8\text{\AA}$ and 4.2\AA . The intensive peaks are found in most X-ray patterns, however one of them is a little shifted. Therefore, the identification is still questionable. The X-ray diffractometer will be calibrated in the critical region and, in addition, infrared spectra will be

run to check the identity.

Both hydrates can be formed at the same time during hydration but one of them is usually dominating. The following factors favor the increase of the amount of hexahydrate:

1. SET-45 hot cement,
2. High water-cement ratio,
3. Long hydration time.

Therefore, the following factors increase the amount of monohydrate:

1. SET-45 cold cement,
2. Low water-cement ratio,
3. Short hydration time.

The most important factor seems to be the choice of the cement. This comes as a surprise because the X-ray patterns of the two dry unhydrated SET-45 cement formulas do not differ significantly and the chemical compositions also seem to be the same. The only reasonable explanation is the difference in MgO grading for the two mixtures as it is described at the examination with optical microscope. Different grading means different specific surface, therefore different surface activity. Water content is also quite important. For example if SET-45 hot cement is hydrated at high water-cement ratio (0.525), only the hexahydrate is formed (Figs. 24-28). However, if low water-cement ratio is used (0.375) both hydrates show up. Changes in the X-ray patterns after one or more days of hydration are slow but definite. For instance, the amount of monohydrate decreases with time and in our case after 7 days totally disappears (Figs. 29-33). The reason for its disappearance is not known yet. The hypothesis is that monohydrate takes up some additional water with time and recrystallizes into hexahydrate.

If SET-45 cold cement is hydrated, the monohydrate is the predominant hydration product and the hexahydrate is formed only to a minor extent.

This is especially true when the water-cement ratio is low (Figs. 34-38) and at early stages of hydration. If there is water available, that is at high-water cement ratio, the time seems to be working in favor of the development of hexahydrate (Figs. 39-43).

When the two cements are mixed in 1:1 ratio, the above statements remain valid. Both hydrates are formed at low water-cement ratio (Figs. 44-48) and no monohydrate is observed (or just a little) at high water-cement ratio (Figs. 49-53).

An addition of borax in the quantity of 1.7% by weight to SET-45 cold cement affects the mechanical properties of the mortar, nevertheless the effect does not show up in the X-ray patterns. The X-ray patterns look very much like the patterns of hydrated SET-45 cold cement alone (Figs. 54-63).

Note that the MgO peak in the X-ray diffraction pattern of ALP cement is much less intensive than that in the SET-45 cements (Fig. 64).

Jet Cement and Pastes

X-ray pattern of Jet cement is similar to the pattern of portland cement Type III (Figs. 65 and 66). The difference appears as few additional diffraction peaks that belong to calcium sulfate (anhydrite) and $C_{11}A_7 \cdot CaF_2$. These two components, not present in ordinary portland cements, contribute to early strength development in regulated-set cements. The rate of consumption of these two components during hydration as well as the amount and quality of the product formed are therefore of special interest. The X-ray patterns of hydrating Jet cement, taken at different early stages of hydration show that ettringite is formed after 40 minutes of hydration (Fig. 67). In the next few hours its amount increases. Ettringite is not the only hydration product, though. X-ray pattern taken after 80 minutes of hydration shows clearly a diffraction peak at $2\theta = 10.2^\circ$ ($d = 8.7\overset{\circ}{A}$) (Fig. 68). This peak is assigned to calcium aluminate hydrate. The identity of another peak at $2\theta = 18.2^\circ$ ($d = 4.85\overset{\circ}{A}$) is somewhat ambiguous. It could belong to monosulfate hydrate but it is present also in X-ray pattern of unhydrated

Jet cement (Fig. 69).

As the hydration proceeds, the diffraction peaks of anhydrite and $C_{11}A_7 \cdot CaF_2$ become weaker. Nevertheless, they are still strong after three hours of hydration (Fig. 70). Even after three days of hydration there is still some unhydrated $C_{11}A_7 \cdot CaF_2$ (Fig. 71). This explains why Jet cement did not develop as high early strengths as the other cements tested. It seems quite possible, however, that the early strengths of this Jet cement can be improved.

Ettringite that yields higher strength than other sulphotoaluminate hydrates is not the only product. Calcium aluminate hydrates and probably monosulfate hydrate are also formed.

6.6 Scanning Electron Microscopy (SEM)

In order to become familiar with the morphological structure of the investigated SET-45 cements, SEM was used. The available time permitted only a limited investigation, nevertheless the results seem useful. JSM-2 (JEOL) SEM equipment was used in the experiments. The results are discussed below.

The SEM investigation was performed with 2000 and 5000 magnifications of the following three days old cement pastes:

SET-45 hot cement	w/c = 0.525
SET-45 cold cement	w/c = 0.525
SET-45 cold + 1.7% borax	w/c = 0.525
SET-45 cold (50%) + SET-45 hot (50%)	w/c = 0.525

It was observed that the samples morphologically differ, each one having some characteristics of its own. For example, there is a noticeable decrease in crystallinity in SET-45 hot paste as compared to SET-45 cold (Figs. 72 and 74). In the latter, extremely well developed crystal forms are observed.

It has been established that the well developed orthorombic single crystal (Fig. 74) is struvite ($\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$). There are not many of them in the SET-45 cold paste. The plates in its vicinity are more typical for the sample. (See also Fig. 75) They have not been identified yet positively but they are probably monohydrate crystals.

SET-45 hot paste is of lower crystallinity (Figs. 72 and 73). Occasional crystals are identified as $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$. They are many in this paste as expected from the corresponding X-ray patterns. It is interesting to mention that they grow in a little different way than in the SET-45 cold paste. Crystal plates, characteristic of SET-45 cold paste are not observed in the SET-45 hot paste. Instead, there is one glassy hydration product that partially covers the particles.

As discussed earlier, an addition of borax to the SET-45 cold does not change the X-ray patterns considerably, however, it has quite an influence on the morphological structure (Figs. 76 and 77). The same crystal types are still observed as in the sample without borax, but the crystals are smaller in size (2 or 3 times). In addition, a new ill-crystalline material is formed that seems to glue the rest of the crystals together. One would conclude that this new feature must increase the strength of the material. However, as it is reported at compressive strength measurements, an addition of borax to SET-45 cold mixture decreases the strength most of the early time.

SEM examination of paste made of SET-45 cold (50%) and SET-45 hot (50%) (Figs. 78 and 79) reveals a combination of morphological characteristics of the two.

To show the differences in morphology between SET-45 and portland cement, Figure 80 shows a SEM photograph of a 1-day old portland cement Type III paste with $w/c = 0.35$. The magnification is 5000. The difference

in morphology is quite obvious. For instance, the chosen area shows a plethora of needle-like crystals in the portland cement paste missing in the SET-45 pastes. These crystals are ettringite and are very characteristic for early strength portland cements rich in aluminate and gypsum.

6.7 Infrared Spectroscopy (IR)

Infrared spectroscopy is frequently used for research and identification purposes in chemistry. Occasionally it has been used also in portland cement chemistry but without any significant success. The reason for this is that the major components of portland cements are silicates which yield similar low resolution infrared spectra consisting of two broad absorption bands. The first band located around 1000 cm^{-1} is a compilation of different stretching modes that involve Si-O bonds. The second band located somewhere around 450 cm^{-1} is a compilation of the corresponding bending modes.

It was hoped that infrared spectra of phosphate cements would be more informative.

Infracord Spectrophotometer (Perkin-Elmer) was used. SET-45 cements were mixed with water and the paste was cured for 7 days. Then the samples were thoroughly ground with a small addition of mineral oil into a fine paste that was placed between two NaCl plates. The plates were then pressed together to get the paste into a thin film.

These specimens were tested when they were 7 days old. The same specimens were also used in X-ray diffraction examination described earlier.

The following cements were used with $w/c = 0.525$ by weight:

SET-45 cold

SET-45 cold + 1.7 borax

SET-45 hot

50% SET-45 cold + 50% SET-45 hot,

The obtained infrared spectra show (Figs. 81-84) that similar problems are encountered with these pastes as with portland cements. The resolution is very low and therefore not much information is provided. Nevertheless, they seem to support the earlier reported X-ray pattern interpretation. For instance, comparing the infrared spectrum of SET-45 hot paste with the infrared spectrums of SET-45 cold paste, it is obvious that the broad absorption band with its maximum around 1000 cm^{-1} for the former sample is symmetrical and for the latter is asymmetrical (Figs. 81 and 82). The symmetrical band implies that only one hydration product is formed. The asymmetrical band with a shoulder implies that at least two hydration products are formed. The main peak is assigned to hexahydrate and the shoulder to monohydrate of ammonium magnesium phosphate. As discussed before, X-ray diffraction analysis gave the same result. The paste made of 50% SET-45 cold and 50% SET-45 hot cements also shows asymmetrical band in its infrared spectrum indicating two hydration products (Fig. 83). An addition of borax does not change the infrared spectrum of SET-45 cold paste (Fig. 84).

7. ANALYSIS AND DISCUSSION OF PHYSICOCHEMICAL TEST RESULTS

7.1 SET-45 Mixtures

SET-45 mixtures are composed of approximately 80% sand and 20% of cementitious material by weight. SET-45 hot mixture also contains a small amount of boric acid which serves as a retarder. The amount is too small to be detected with X-ray diffraction method. However, it has been detected with optical microscopy. The concentration of the retarder's particles is the largest in the #30 - #50 and #50 - #100 size fractions. They were found to dissolve in water at the same rate as borax. The manufacturer identified them as boric acid.

7.2 SET-45 Cement

The cementitious material, that is material passing sieve #200, is composed of two phases. One phase is magnesium oxide (MgO). The magnesium oxide phase in SET-45 cold cement is finer, that is the particles are a few times smaller in size than the particles of MgO in SET-45 hot cement. The other phase is ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$). It looks the same in both SET-45 formula and passes sieve no. 200 but a small part conglomerates into big white chunks that are observed in SET-45 mixtures occasionally.

7.3 SET-45 Pastes

When SET-45 cements are mixed with water the pastes set fast, within a few minutes almost independently of the water-cement ratio. This is true for both SET-45 formulas indicating the absence of retarder in the material passing sieve #200.

The hydration is fast. The $\text{NH}_4\text{H}_2\text{PO}_4$ is dissolved and used up fast, at least within the first hour of hydration and probably sooner (Figs. 23-62). Magnesium oxide, on the other hand, reacts only partially and its presence is detected even after 7 days of hydration (Figs. 27, 32, 37 and 42). This indicates that a larger amount of MgO is added than needed for chemical reactions.

Two major hydration products have been observed and identified. One is ammonium magnesium phosphate hexahydrate ($\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$) or shortly hexahydrate; the other is ammonium magnesium phosphate monohydrate ($\text{NH}_4\text{MgPO}_4 \cdot \text{H}_2\text{O}$) or shortly monohydrate. Some other hydrates might be formed but in a lesser amount. This remains to be determined in the future.

Hexa- and monohydrates are formed in different proportions or ratios depending on which SET-45 formula is used. It also depends on the water-cement ratio, and hydration time. For instance, SET-45 hot cement with high water-cement ratio produces almost exclusively hexahydrate only. This is

demonstrated in Figure 81 where the infrared spectrum of a 7 days old SET-45 hot paste prepared with water-cement ratio 0.525 yields a single symmetrical absorption band around 1000 cm^{-1} . This is an indicator of a single phosphate. X-ray pattern of the same paste confirms the existence of a single product identified as hexahydrate (Fig. 28).

On the other hand SET-45 cold paste at the same age and with the same water-cement ratio produces both hexa- and monohydrates. This is shown by a shoulder attached to the symmetrical absorption band in the infrared spectra (Fig. 82) thus indicating at least two hydration products. The corresponding X-ray diffraction patterns confirm this. The additional product is identified as monohydrate (Fig. 43).

At low water-cement ratio, the hot weather formula produces both monohydrate and hexahydrate at the beginning of the hydration. Later, the monohydrate gradually disappears which may be attributed to recrystallization into hexahydrate. A typical example for this can be a hot weather paste with the water-cement ratio of 0.375 by weight which shows some monohydrate after 3 days of hydration but only hexahydrate after 7 days (Figs. 32 and 33). This indicates recrystallization the reason for which is that the hexahydrate is thermodynamically more stable form; therefore it is the final hydration product if there is enough moisture and time for the process to be completed. This latter statement is important and should be carefully examined and checked out in the future. This is so because when monohydrate transforms with time into hexahydrate, the new crystal has a greater volume which could cause troubles in the already hardened SET-45 mortar or paste. As a matter of fact, 7 days old cylinders prepared with SET-45 cold mixture and water content of 8% or higher of the weight of the dry mixture cracked when cured in a fog room (Fig. 20). The reason for cracking could just be the mentioned mono-hexa transformation. Mortars with 8% and higher water contents have

enough moisture for the transformation to take place and mortars prepared at lower ratios do not in the case of wet curing. High alumina cements are a well known example where the originally formed hexagonal aluminate hydrate recrystallizes into the more stable cubic aluminate hydrate under wet curing. This process also causes loss in strength.

It has been established that an addition of borax to SET-45 cold mixture retards the setting during hydration. As a side effect, it also increases the fluidity of the mortar. The mechanism is not known. Otherwise the major hydration products of hydrated SET-45 cold cement are independent of the presence of borax as seen from the X-ray patterns (Figs. 54-63). Even the mono-hexa ratio remains unchanged despite the fact that borates and phosphates can form complexes. Further research is needed to get some better understanding of the role of borax. Borax, however, does change the morphology of the hydration products as seen on electron microscope (Figs. 76 and 77). The crystals get smaller in size and the hydrated product becomes ill-crystalline or even amorphous. This may influence the early strength development.

When SET-45 hot and SET-45 cold cements are mixed together, X-ray patterns of the hydrated pastes look like the average of pastes prepared only with SET-45 cold cement and pastes prepared only with SET-45 hot cement (Figs. 44-53). Knowing that with an addition of SET-45 hot mixture to SET-45 cold mixture a similar retarding effect is achieved as with an addition of borax to SET-45 cold mixture, this became interesting. Namely, it means that although the same retarding effect is obtained with the blending, the mono-hexa ratio of the hydration products is not the same. As mentioned before, an addition of borax does not change the mono-hexa ratio in hydrating SET-45 cold cement. However, an addition of SET-45 hot cement to the SET-45 cold cement does increase the amount of hexahydrate. Accordingly, the amount of

monohydrate is lowered and the danger of cracking is lowered too. For the time being no studies have been done yet in this direction.

Another possibility to increase formation of hexahydrate in hydrating SET-45 cold cement is based on experiments performed by T. Sugaman and L. E. Kukacka. From their results an addition of ammonium polyphosphate solution to the mixing water should reduce the mono-hexa ratio. This approach also requires further investigation.

7.4 A&P (Aluminum Phosphate) Mixtures

The cementitious material in the A&P mixture is again magnesium oxide (MgO) based, nevertheless its chemistry differs from the SET-45 mixtures. A water-soluble phosphate is used for hydration in this formulation which is aluminum dihydrogen phosphate ($\text{Al}(\text{H}_2\text{PO}_4)_3$) in 50% concentrations. This solution is very acidic ($\text{pH} = 1.3$), viscous ($\eta = 27$ cp at $T = 23^\circ\text{C}$), and dense ($\rho_{\text{rel}}^{23^\circ\text{C}} = 1.49$).

The solid component is a mixture of sand, fly ash, and magnesium oxide. The material passing sieve no. 200, that is the material referred to as cement in this report, is also a mixture of sand, fly ash and magnesium oxide. It is not as homogeneous as the SET-45 cement. Compared to SET-45 cements, the amount of magnesium oxide phase is relatively small (Figs. 21, 22 and 64).

The mortars and pastes, as the liquid itself, are viscous and acidic. Although the acidity decreases as the hydration progresses, the process of neutralization is slow (Section 6.4). Therefore the mortars are not recommended to be placed on a carbonate base without any protective surface preparation. The composition of the hydration product is not known yet. It is a strong mass of ill-crystallinity or no crystallinity at all. As described in Section 6.3, the mass is formed between the particles of sand, fly ash, and unreacted MgO and glues them together.

7.5 Onoda Jet Cement

The high-early-strength producing components of the Jet cement are $C_{11}A_7 \cdot CaF_2$ and $CaSO_4$ (anhydrite) forming different aluminate-and sulfo-aluminate-hydrates when mixed with water. Both components were detected in X-ray pattern of Jet cement along with their consumption during hydration (Figs. 66-71). For instance, some unhydrated $C_{11}A_7 \cdot CaF_2$ is observed even after 3 days of hydration (Fig. 71). The main products are ettringite and monosulfate hydrate. Ettringite is favored at early stages and monosulfate hydrate at later stages after all the anhydrite is used up. Presence of calcium carbonate is also detected ($2\theta = 29^\circ$) (Fig. 66). As reported, an addition of calcium carbonate improves the initial strength without influence on setting of the Jet cement. Presence of sodium borates is also possible ($2\theta = 30^\circ$). They increase the formation of monosulfate and, at the same time, decrease the formation of ettringite, thus decreasing the early strength.

Although Jet cement is not recommended for emergency repairs because of its low early strengths, regulated-set cements are considered worthwhile to be studied in the future. The chemistry of the hydration processes is reasonably well known as well as the effects of different modifications and admixtures.

8. COMPARISON OF THE TESTED MATERIALS

Based on the results obtained up to this point of testing, the advantages and disadvantages of each material under investigation can be summarized, as follows:

1. The same water content under identical conditions produces the lowest viscosity in SET-45 hot formula, and the highest viscosity in the AlP mixtures. (Tables 1 and 6)

2. SET-45 cold formula has the shortest setting times (initial set is less than 10 minutes, final set is less than 15 minutes at room temperature), and SET-45 hot formula has the longest ones. The setting times of the other tested mixtures fall between these two extremes. (Figs. 4 and 5)

3. The highest compressive strengths at the ages of 1 and 3 hours are developed by SET-45 cold weather mortar. The measured 1-hour strength, for instance, was more than 5,000 psi with 10% water (flowing consistency) at room temperature which is perhaps unnecessarily high strength for the given purpose (Fig. 9). Another advantage is that this material does not require wet curing. On the other hand, its setting times are the shortest, initial setting being less than 10 minutes at room temperature and probably much less at elevated temperatures. Also this is the material that has the tendency to convert the monohydrate to hexahydrate with the potentiality of causing cracking in a week or so in the hardened mortar. Finally, this material develops the most heat within a few hours.

4. The SET-45 hot weather mortar has much longer setting times and develops less heat due to the presence of boric acid. However, it produces little strength at room temperature during the first 3 hours. It is very likely that at elevated temperatures the early strengths as well as setting and heat development will be similar to those of the cold weather formula at room temperature. The exact behavior will be investigated in the coming months.

5. The modified SET-45 cold weather mortars, that is, the 50-50 blend of cold weather-hot weather formulas, as well as the cold weather formula with borax addition, seem to combine the advantages of the two individual formulas. For this reason these materials will be closely examined further in the coming months.

6. The A&P mortars can reach compressive strengths in excess of 3,000 psi at the age of 3 hours despite the fact that their 1-hour strengths are quite low. The setting times are similar to those of the modified SET-45 cold weather mortars. The behavior of this material at higher and lower temperatures as well as a tendency for recrystallization are not known at this time. (Tables 12 and 13)

7. The Jet cement mortars can develop about 1500 psi strengths at the age of 3 hours, and considerably less by 1 hour at room temperature. The setting times are similar to those of the A&P mortars. Otherwise the behavior of this cement is expected to be the closest to portland cement. (Table 14)

9. FUTURE WORK

The work during the concluding six months of the project will concentrate on the indepth investigation of various SET-45 formulas but the A&P mixture will also be tested to a certain extent.

All mortars will have fluid consistency. Combinations of mechanical and physicochemical tests will be used again.

The testing of the following mechanical properties is planned:

1. Effects of water-reducing admixtures, such as organosilicons
2. Compressive and flexural strengths at room temperature up to 90 days
3. Setting times and early compressive strengths with specimens made with heated and unheated mixing water, and cured at a temperature around freezing point
4. Setting times and early compressive strengths with specimens made with cooled and uncooled mixing water, and cured at 100°F
5. Shrinkage
6. Water absorption
7. Bond to old portland cement concrete.

In the physicochemical investigations again optical and electron microscopy, X-ray diffraction, and infrared spectroscopy will be used. The investigation will concentrate on the modification and optimization of the SET-45 formulas. Among others, the following items will be investigated:

1. Hydration and hydration products of the different formulas
2. Recrystallization process of the monohydrate and its reduction
3. Increase of time of setting at high temperatures without hurting the early strengths too much
4. Increase of early strengths at low temperatures by admixtures
5. Reduction of the rate and quantity of the early heat development without hurting the early strengths
6. Effects of chemical admixtures (ammonium polyphosphate, etc.) on the properties of SET-45 mortars, especially effects of cations having complexing abilities.

A preparation of the final report will conclude the project.

10. CONCLUSIONS

It is not a problem to produce compressive strengths in excess of 2000 psi after 1-hour at room temperature. After all the SET-45 cold weather formula has approximately 5000 psi strength even with flowing consistency. The problem is the shortness of the time of setting of this formula. This problem is even more severe at elevated temperatures.

Fortunately the 1-hour strength of the cold formula is so high that it leaves place for compromises in several directions based on further research. Such research can be built on the insight that our physicochemical investigation provided into the hydration of the SET-45 formulas. This way it may be possible to increase the time of setting by a suitable admixture, or by a higher water content, or by a higher sand content, or by a combination of these, and still achieve the needed 2000 psi strength at the age of

1-hour. If further research in these directions remains still unsuccessful, special construction technique should be used. Such a technique is to mix the SET-45 formula as a flowing mixture in a movable mixer and pouring it immediately into the damaged area.

Low ambient temperatures may cause the opposite problem, namely inadequate early strengths. This problem will be faced in the second half of this project.

TABLE 1 - Compositions of SET-45 Mixtures with High [10% by weight] Water Content

Mix designation	Quantity of Materials, g			
	Cold mixture	Hot mixture	Borax	Water
SC1	5000	-	-	500
SH1	-	5000	-	500
SCH1	2500	2500	-	500
SCB1	5000	-	17	500

TABLE 2 - Compositions of SET-45 Mixtures with Medium [8% by weight] Water Content

Mix designation	Quantity of Materials, g			
	Cold mixture	Hot mixture	Borax	Water
SC2	5000	-	-	400
SH2	-	5000	-	400
SCH2	2500	2500	-	400
SCB2	5000	-	17	400

TABLE 3 - Compositions of SET-45 Mixtures with Low [5.5% by weight] Water Content

Mix designation	Quantity of Materials, g			
	Cold mixture	Hot mixture	Admixtures borax	Water
SC3	5000	-	-	275
SH3	-	5000	-	275
SCH3	2500	2500	-	275
SCB3	5000	-	17	275

TABLE 4 - Compositions of SET-45 Cold Mixtures with Admixtures

Mix designation	Quantity of Materials, g			
	Cold mixture	Admixtures		Water
		Plastocrete 161R	Epoxy	
SS4	5000	100	-	350 (7% by weight)
SE4	12000	-	Curing Agent 110.5 Resin 729.5	450 (3.75% by weight)

TABLE 5 - Compositions of A&P Concretes

Mix designation	Quantity of Materials, g			
	Alp mixture	Alp solution	Water	Liquid
DA5	5000	618	-	618 (12.36%)
DAS5	5000	618	-	618 (12.36%)
DASW5	5000	580	38	618 (12.36%)
DAW5	5000	580	68	648 (12.96%)

TABLE 6 - Compositions of A&P Mortars

Mix designation	Quantity of Materials, g			
	Alp mixture	Admixtures Alp solution	Water	Liquid
DAA6	5000	790	-	790 (15.8%)
DAB6	5000	824	-	824 (16.48%)
DAC6	5000	900	-	900 (18.0%)
DAW6	5000	824	38	862 (17.24%)
DAWB6	5000	824	76	900 (18.0%)

TABLE 7 - Compositions of Jet Mortars

Mix designation	Quantity of Materials, g				
	Jet Cement	Superplasticizer	Fine sand*	Coarse sand**	Water
JW7	1000	-	2400	1600	500 (10%)
JWA7	1000	-	2400	1600	680 (13.6%)
JWM7	1000	Mighty 150 30	2400	1600	650 (13%)
JWB7	1000	Pozzolith 200-XR 30	2400	1600	650 (13%)

*Passing sieve #16

**Passing sieve #4 and retained on #16.

TABLE 8 - Properties of SET-45 Mortars with High (10% by weight) Water Content*

Mix designation	Properties of Fresh Mortar			Compressive strength, psi		
	Flow %	Setting time		1 Hr	3 Hr	24 Hr
		Initial	Final			
SC1	145.9	9 min 45 sec	13 min 30 sec	5640	7050	7110
SH1	150	40 min	47 min	-***	1670	6540
SCH1	148.7	15 min	18 min 30 sec	3150	6350	7420
SCB1	149.5	17 min	21 min	2790	5250	5920

*Compositions are presented in Table 1.

TABLE 9 - Properties of SET-45 Mortars with Medium (8% by weight) Water Content**

Mix designation	Properties of Fresh Mortar			Compressive strength, psi		
	Flow %	Setting Time		1 Hr	3 Hr	24 Hr
		Initial	Final			
SC2	111.3	9 min	11 min 45 sec	6100	11060	12130
SH2	109.3	49 min	60 min	-***	1930	9080
SCH2	101.6	29 min 30 sec	33 min 30 sec	-***	4710	10130
SCB2	106.0	19 min	21 min 30 sec	1090	5040	8000

**Compositions are presented in Table 2.

***One-hour tests could not be performed, because specimens were weak to remove from the mold.

TABLE 10 - Properties of SET-45 Mortars with Low (5.5% by weight) Water Content

Mix designation	Properties of Fresh Mortar			Compressive strength, psi		
	Flow %	Setting Time		1 Hr	3 Hr	24 Hr
		Initial	Final			
SC3	28	6 min 30 sec	8 min 30 sec	10140	11690	11940
SH3	19.7	30 min 30 sec	36 min	-**	3570	8900
SCH3	28.4	18 min	20 min 15 sec	2640	8180	11810
SCB3	27.3	17 min 45 sec	22 min	3100	10690	11590

*Compositions are presented in Table 3.

**1-Hr test could not be performed, because the specimens were weak to remove from the mold.

TABLE 11 - Properties of SET-45 Cold Mortars with Admixtures*

Mix designation	Properties of Fresh Mortar			Compressive strength, psi		
	Flow %	Setting Time		1 Hr	3 Hr	24 Hr
		Initial	Final			
SS4	107.3	13 min	16 min 30 sec	2890	3810	-**
SE4	15.3	11 min 15 sec	20 min	780	1580	2110

*Compositions are presented in Table 4.

**24-Hr test could not be performed, because the specimens were broken while demolding.

TABLE 12 - Properties of Aluminum Phosphate Concretes*

Mix designation	Properties of Fresh Concrete			Compressive strength, psi		
	Flow %	Setting Time				
		Initial	Final	1 Hr	3 Hr	24 Hr
DA5	50.8	19 min	22 min	400	1830	6980
DAS5	45.4	14 min 30 sec	19 min	560	2520	6930
DASW5	52.9	14 min	18 min	340	2340	3350
DAW5	73.3	19 min	30 min	310	1360	4540

*Compositions are presented in Table 5.

TABLE 13 - Properties of Aluminum Phosphate Mortars*

Mix designation	Properties of Fresh Mortar			Compressive strength, psi		
	Flow %	Setting Time				
		Initial	Final	1 Hr	3 Hr	24 Hr
DA6	77.3	23 min 14 sec	26 min	430	1930	7240
DAB6	93.2	22 min	25 min	220	720	5690
DAC6	91.3	14 min 15 sec	19 min	330	2080	6540
DAW6	96.7	13 min 30 sec	16 min 30 sec	610	3140	5410
DAWB6	110.8	17 min	19 min 45 sec	370	3320	5325

*Compositions are presented in Table 6.

TABLE 14 - Properties of Jet Mortars**

Mix designation	Properties of Plastic Concrete					
	Flow%	Setting Time		Compressive strength, psi		
		Initial	Final	1 Hr	3 Hr	24 Hr
JW7	5.1	6 min 30 sec	14 min	1190	2600	4420
JWA7	75.5	12 min 45 sec	26 min 10 sec	450	1560	2760
JWM7	140	24 min	41 min	210	1680	2710
JWB7	137	73 min	-	-*	20	1780

*One hour test could not be performed, because the specimens were too weak to remove from the mold.

**Compositions are presented in Table 7.

TABLE 15 - Properties of SET-45 Cold Mortars as a Function of the Water Content

The strength specimens were 2" x 4" cylinders.

Mix Designation	Water* %	Flow %	Compressive Strength, psi					
			1 Hr	3 Hrs	1 Day	7 Days	28 Days	90 Days
ASC1	6.0	36.3	7320	9150	8410	8000	8260	9280
ASC2	6.5	50.0	7290	8700	8560	8240	7500	8550
ASC3	7.0	66.0	7550	8210	8770	8400	7860	8180
ASC4	7.27	84.4	7870	8160	8740	8340	8320	8310
ASC5	8.0	102.7	6240	6150	8090	7710	6580	6820
ASC6	8.5	114.5	5850	5620	6950	5920	5540	5730
ASC7	9.0	131.3	4660	5110	5600	5470	4870	6050
ASC8	9.5	133.6	4510	4500	4810	4630	4520	6190
ASC9	10.0	140.6	3910	3960	4670	4140	4160	6400
ASC10	10.5	145.3	2610	2800	3280	3330	3220	-
ASC11	11.0	150.0	2490	2840	3230	3000	2940	4580

*Percent by weight of the dry mixture.

TABLE 16 - Properties of SET-45 Hot Mortars as a Function of the Water Content

The strength specimens were 2" x 4" cylinders.

Mix Designation	Water* %	Flow %	Compressive Strength, psi					
			1 Hr	3 Hrs	1 Day	7 Days	28 Days	90 Days
ASH1	5.0	14.5	**	3320	6880	7910	8210	9530
ASH2	5.5	43.4	1460	4660	7800	8470	7640	8340
ASH3	6.0	55.5	**	2390	6570	7000	7590	8130
ASH4	6.5	68.8	**	3050	8010	8100	8820	8300
ASH5	7.0	94.5	**	3010	7610	7460	7470	8020
ASH6	7.5	103.0	**	3836	7090	7980	8085	8240
ASH7	8.0	124.0	**	2500	5600	6400	6690	6900
ASH8	8.5	126.6	**	4650	7920	7660	7770	8180
ASH9	9	143.0	**	2360	4950	4990	5510	6370
ASH10	9.5	148.1	**	2140	3920	4860	5410	6490
ASH11	10.0	150.0	**	1640	3440	3820	4110	5460

*Percent by weight of the dry mixture.

**One hour tests could not be performed, because specimens were too weak to remove from the mold.

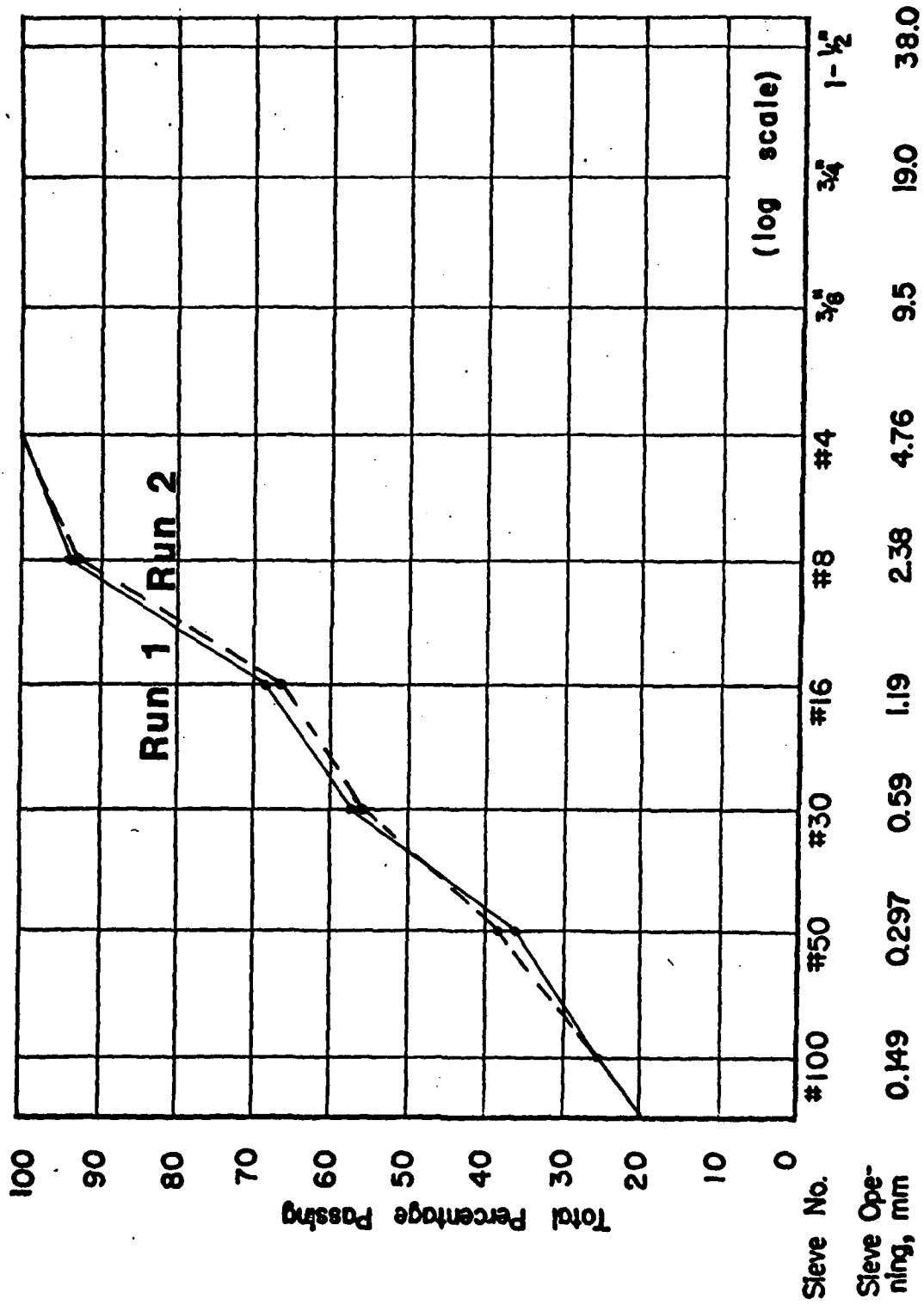


Fig. 1 - Grading of SET-45 hot formula.

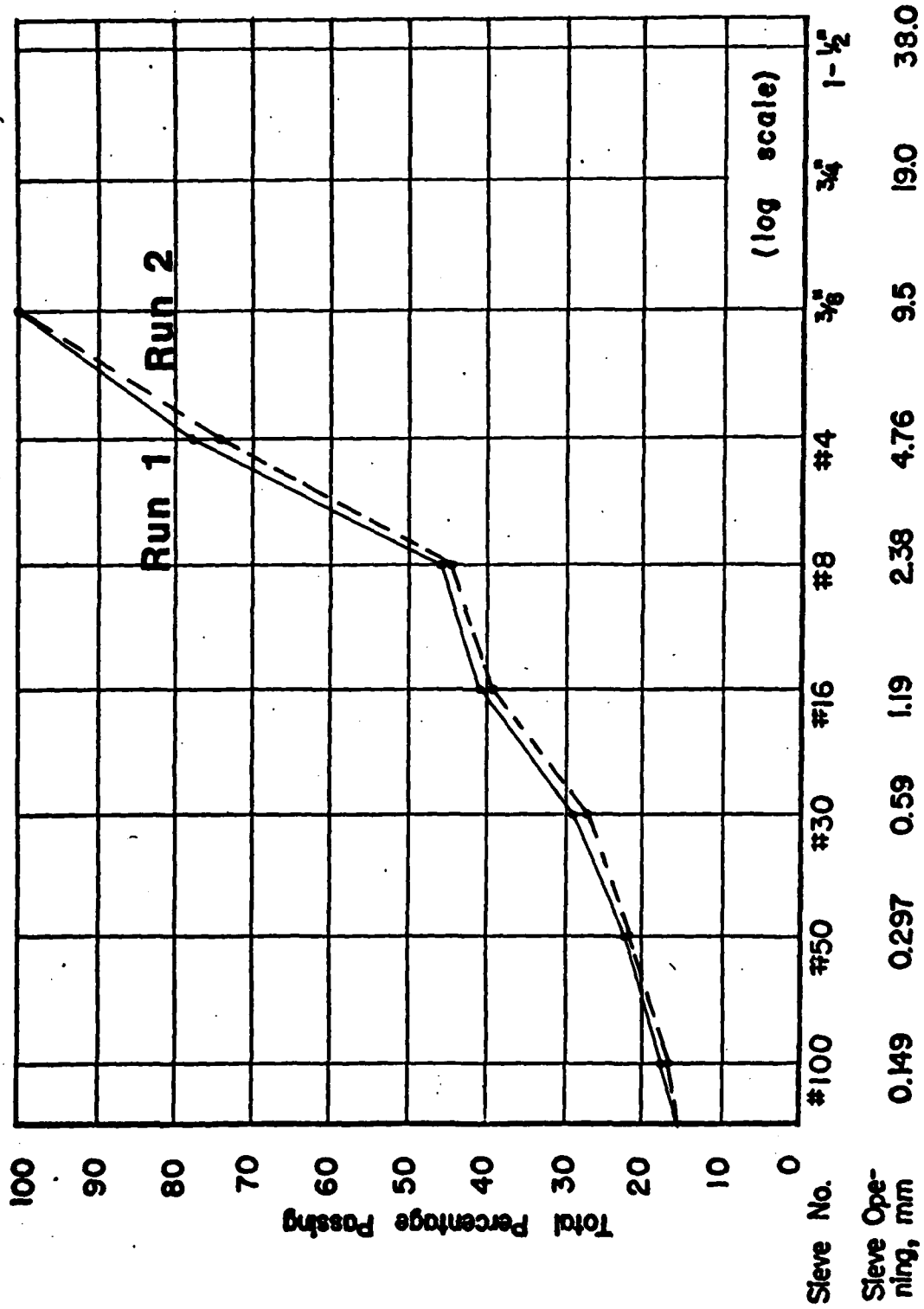


Fig. 2 - Grading of aluminum phosphate mixture

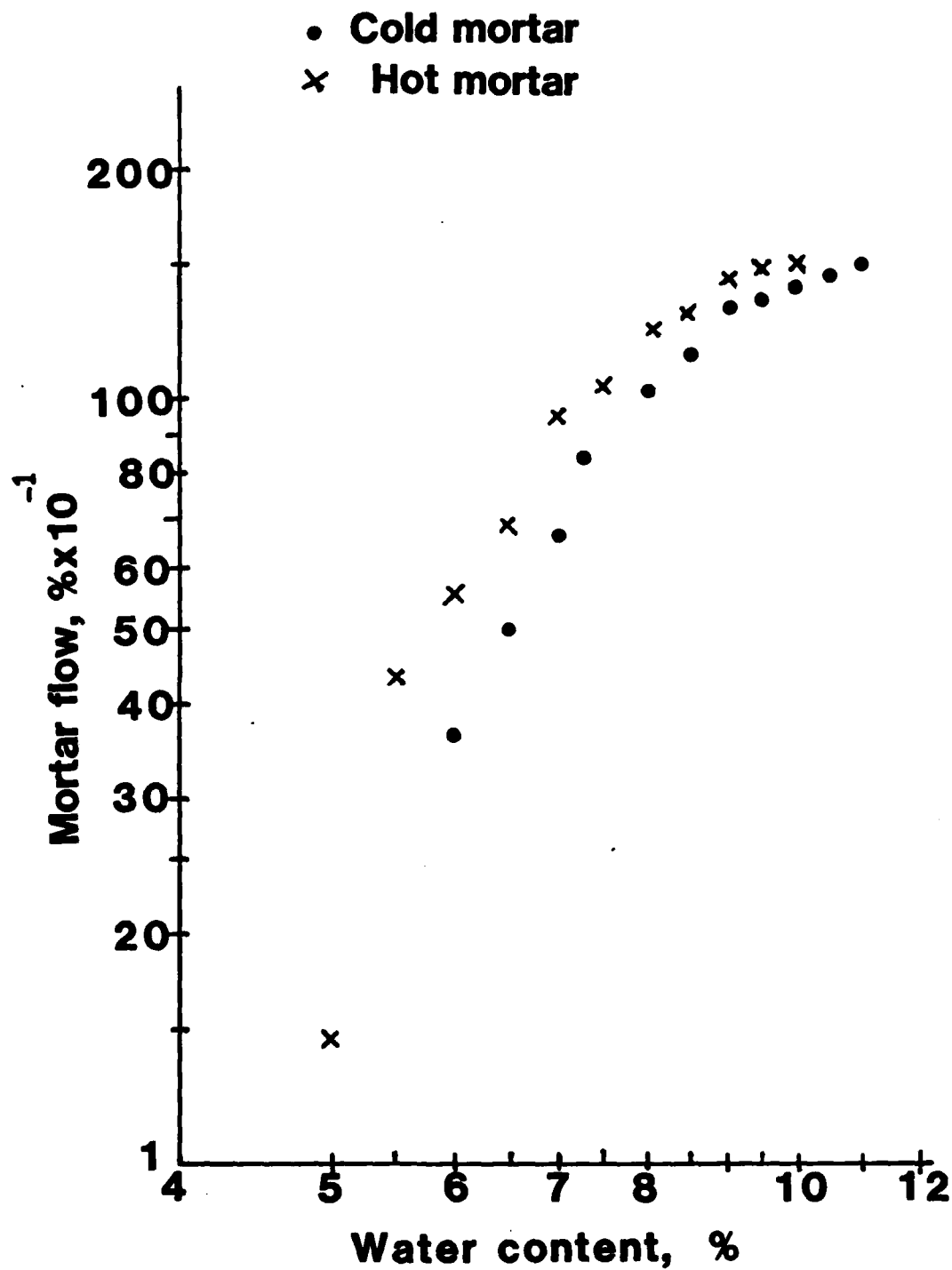


Fig. 3 - Standard flow of SET-45 mortars as a function of water content

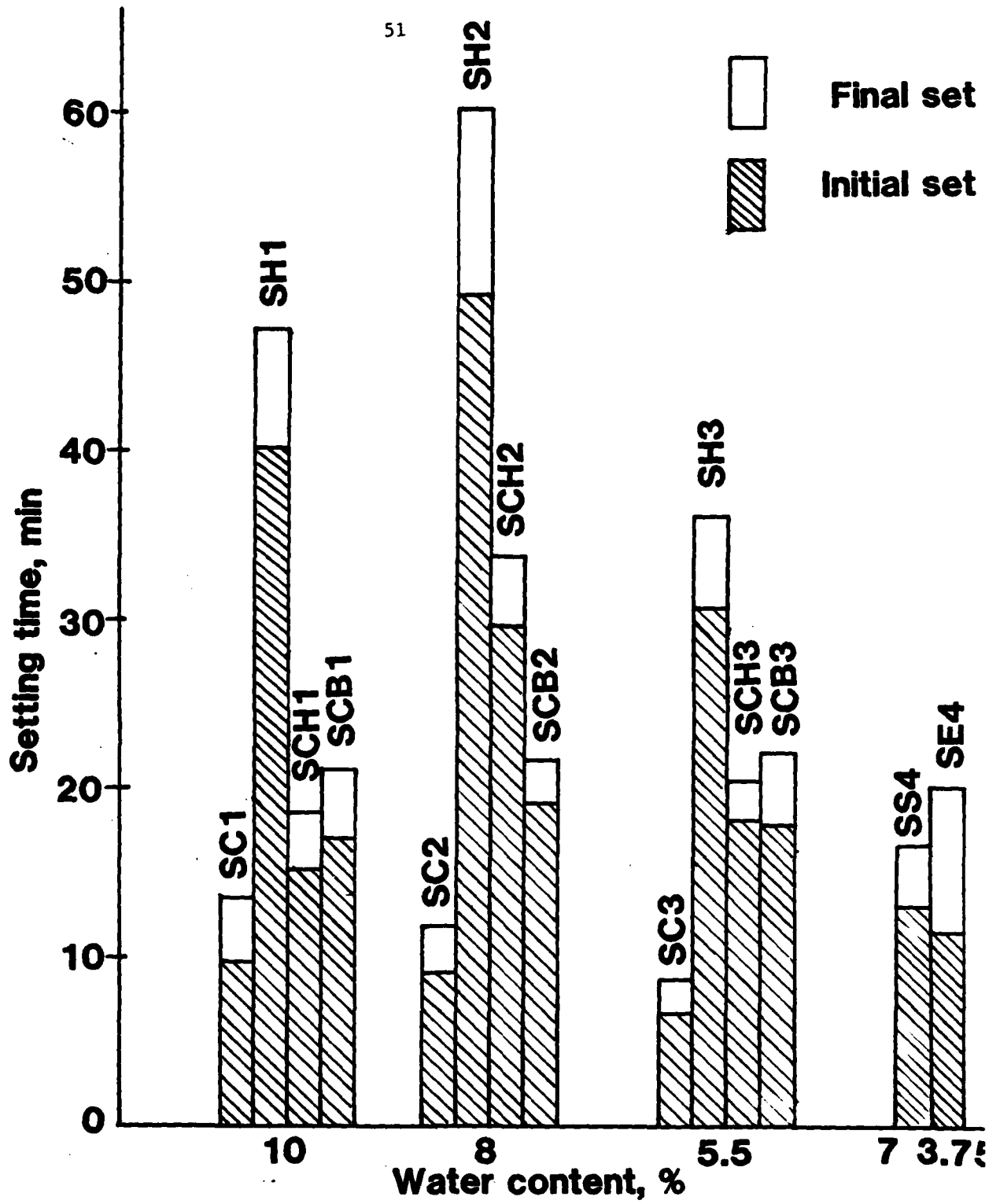


Fig. 4 - Setting time of SET-45 mortars as a function of water content

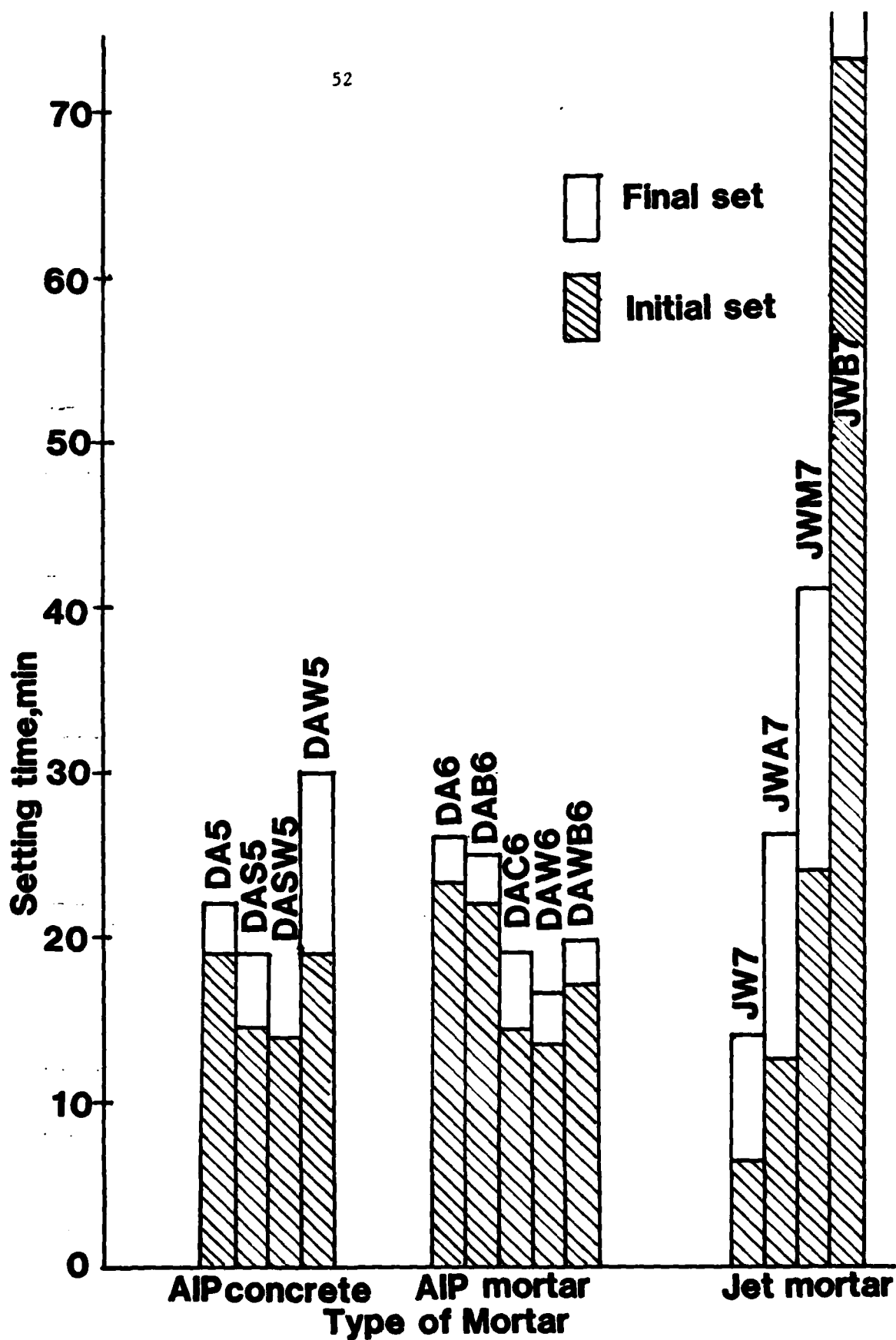


Fig.5 - Setting times of aluminum phosphate mortars and Jet cement mortars

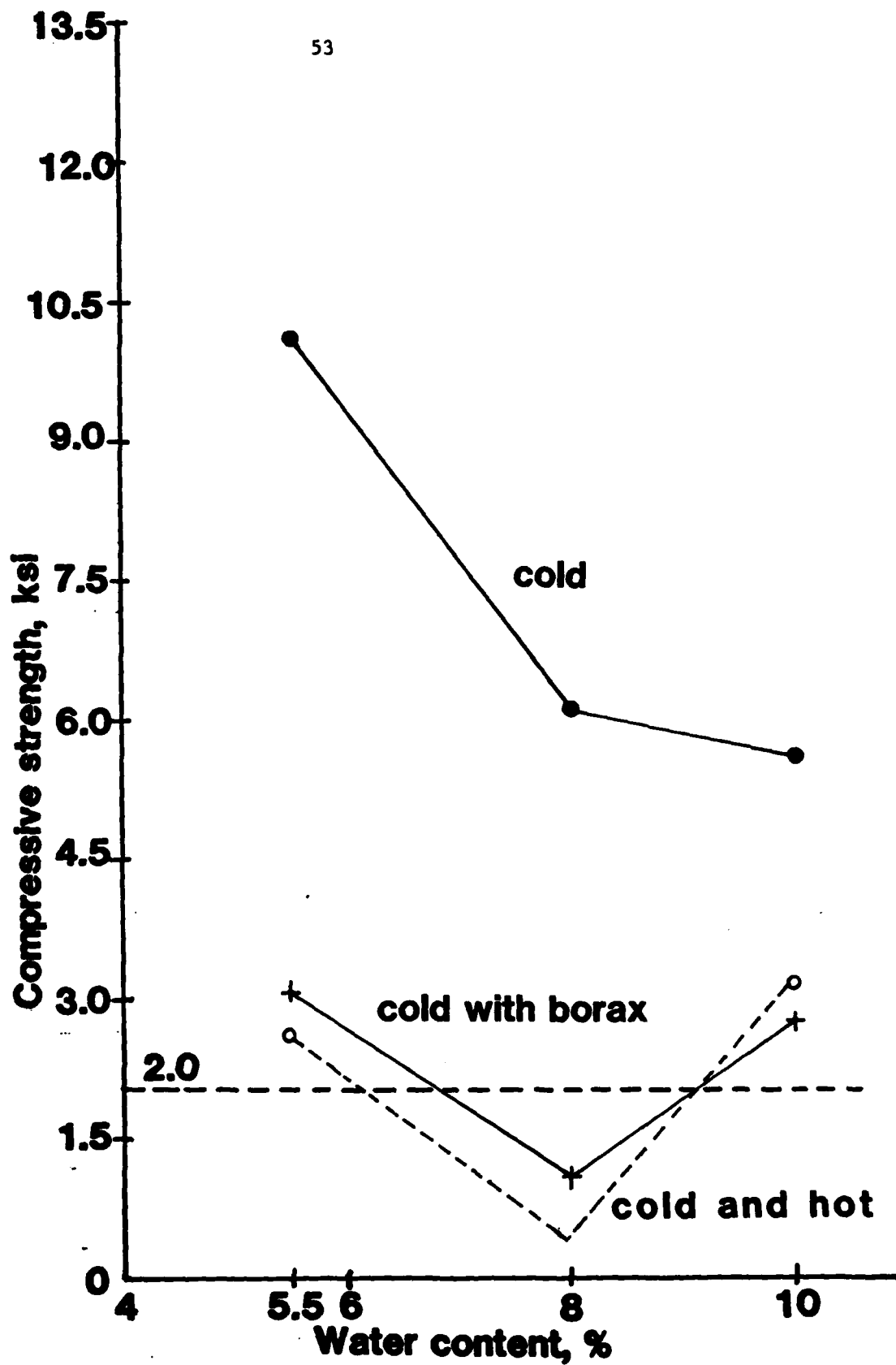


Fig. 6 - Comparison of compressive strengths at 1 hour for SET-45 mortars at various water contents

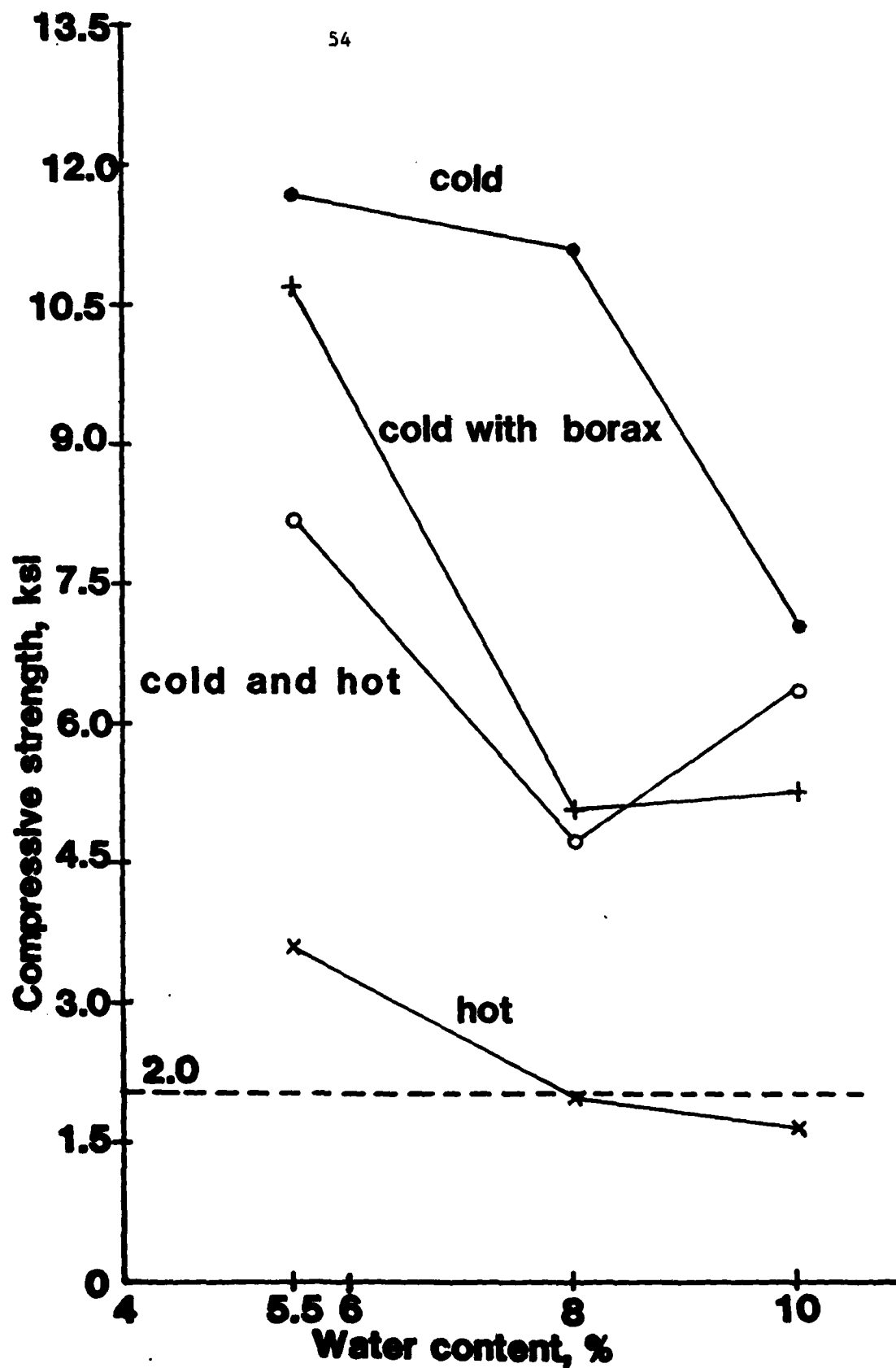


Fig. 7 - Comparison of compressive strengths at 3 hours for various SET-45 mortars at various water contents

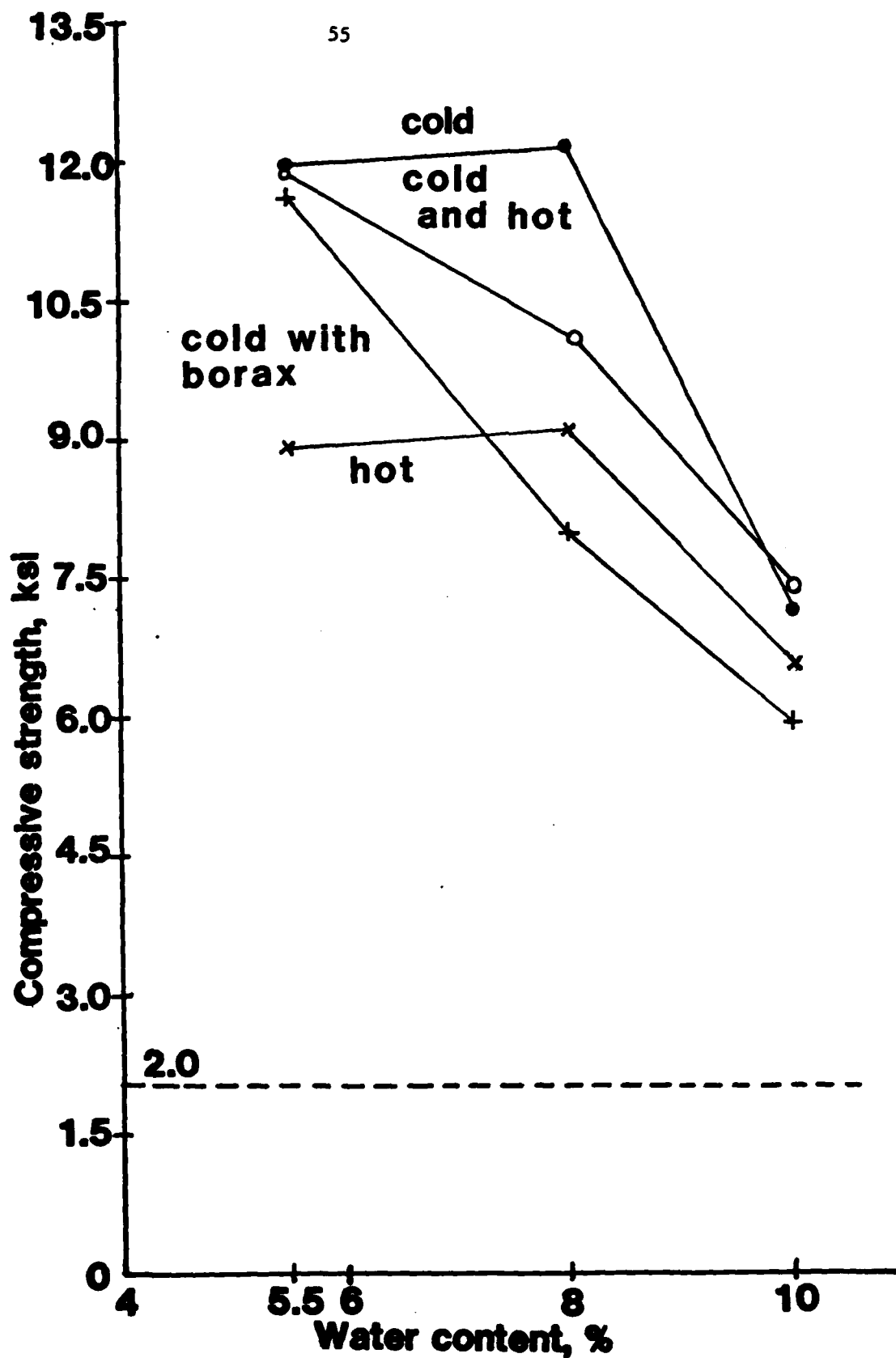


Fig. 8 - Comparison of Compressive strengths at 24 hours for SET-45 mortars at various water contents

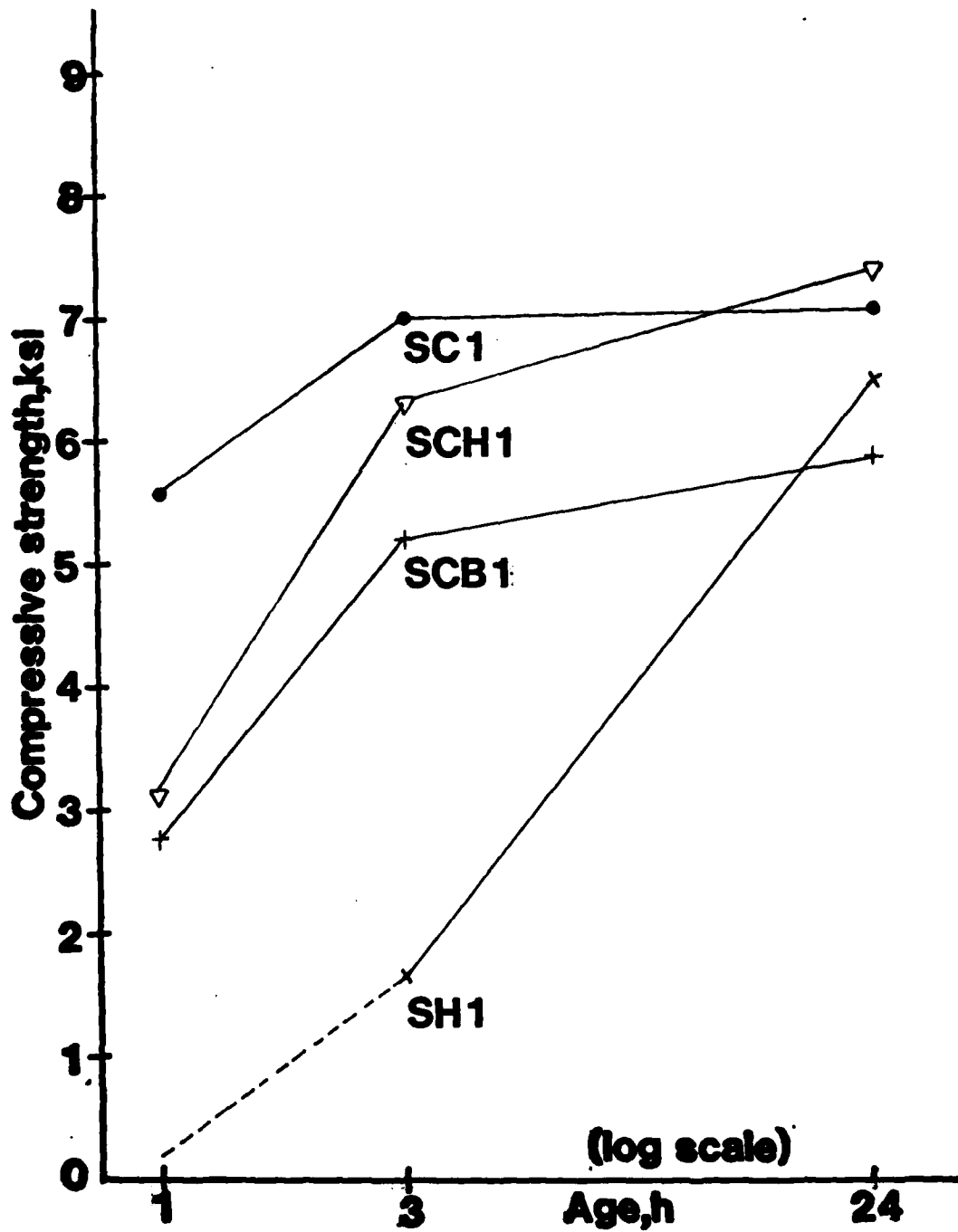


Fig. 9 - Relationship between compressive strength and early age of SET-45 mortars with high (10%) water content

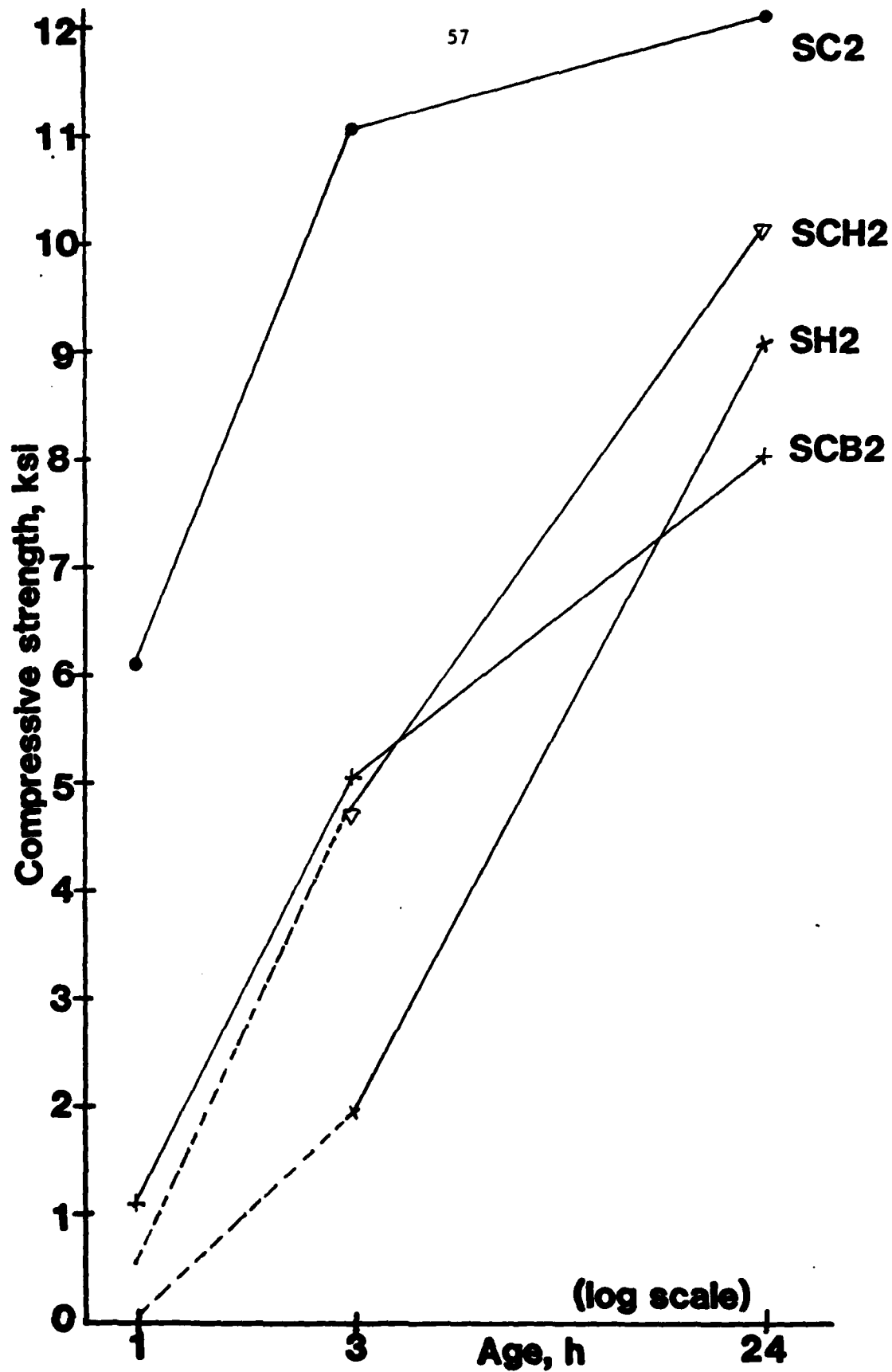


Fig. 10 - Relationship between compressive strength and early age of SET-45 mortars with medium (8%) water content

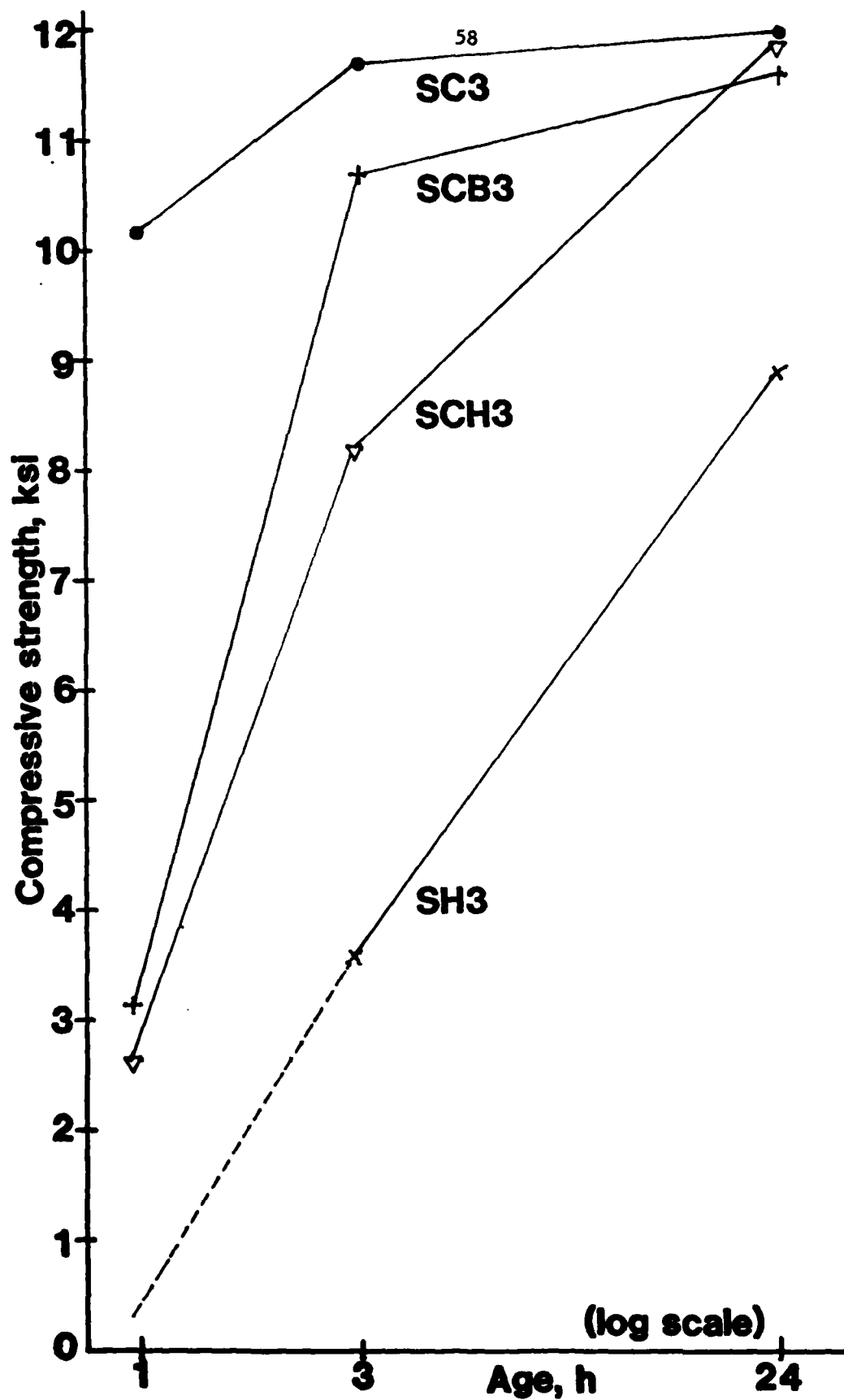


Fig. 11 - Relationship between compressive strength and early age of SET-45 mortars with low (5.5%) water content

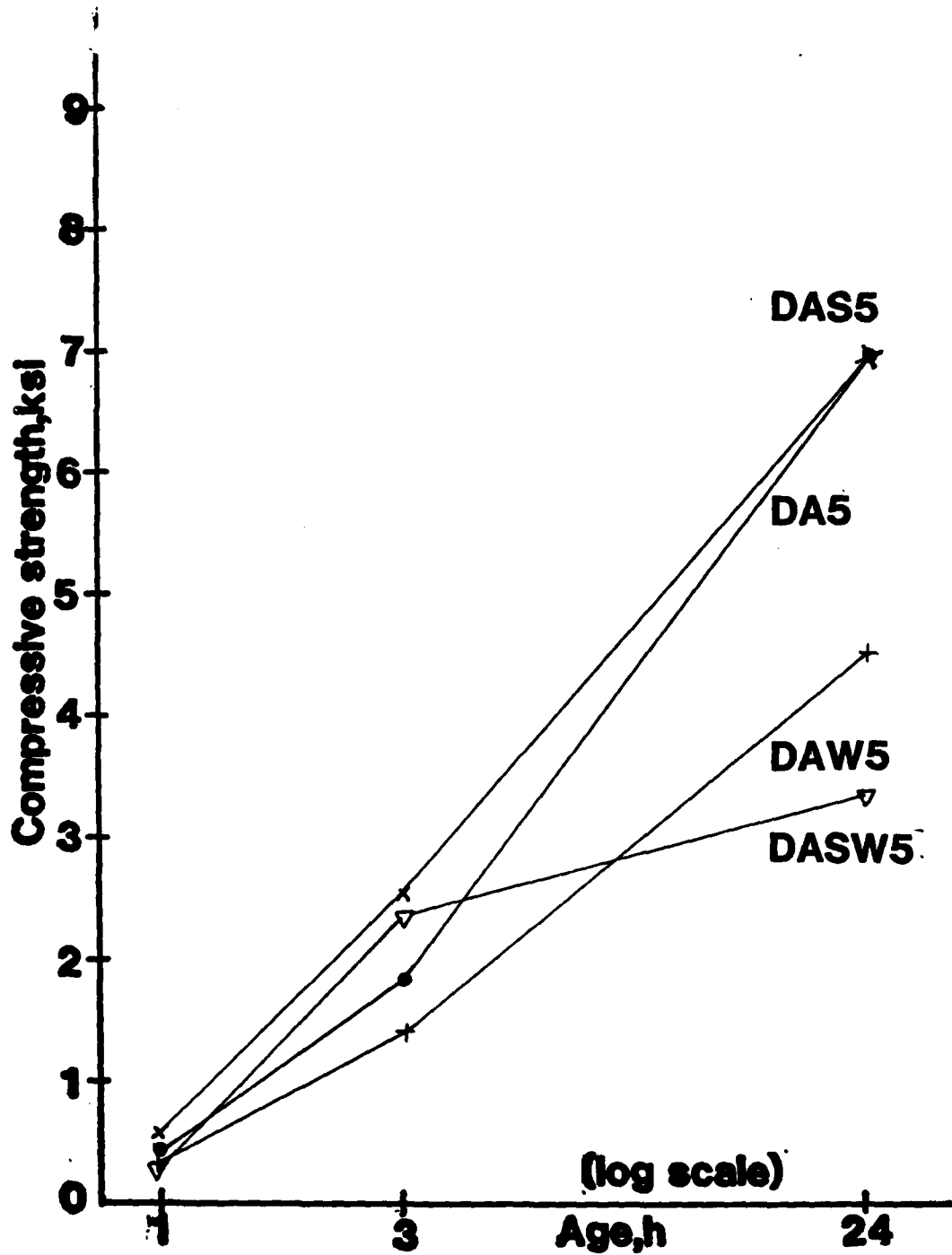


Fig. 12 - Relationship between compressive strength and early age of A1p concrete

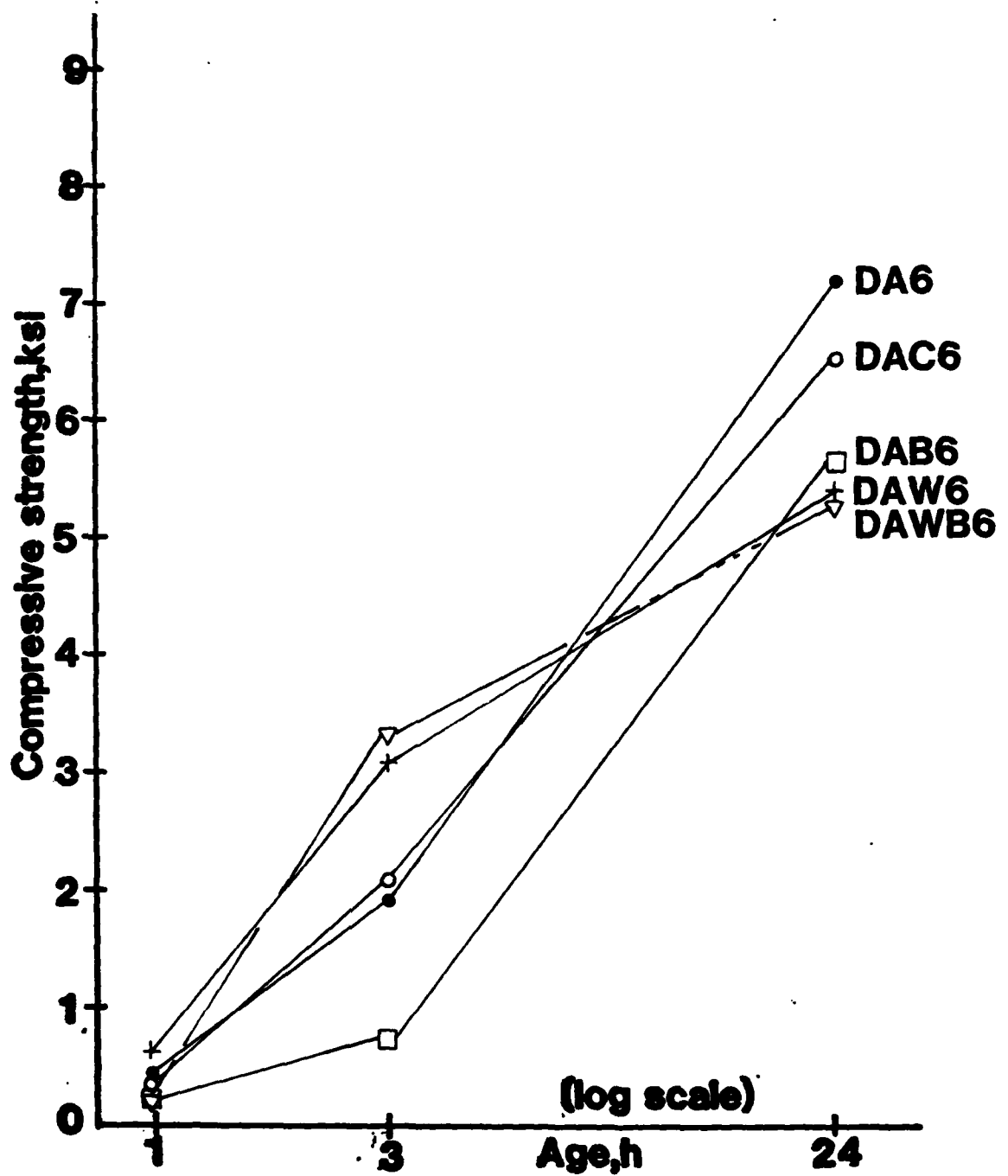


Fig. 13 - Relationship between compressive strength and early age of Alp mortar

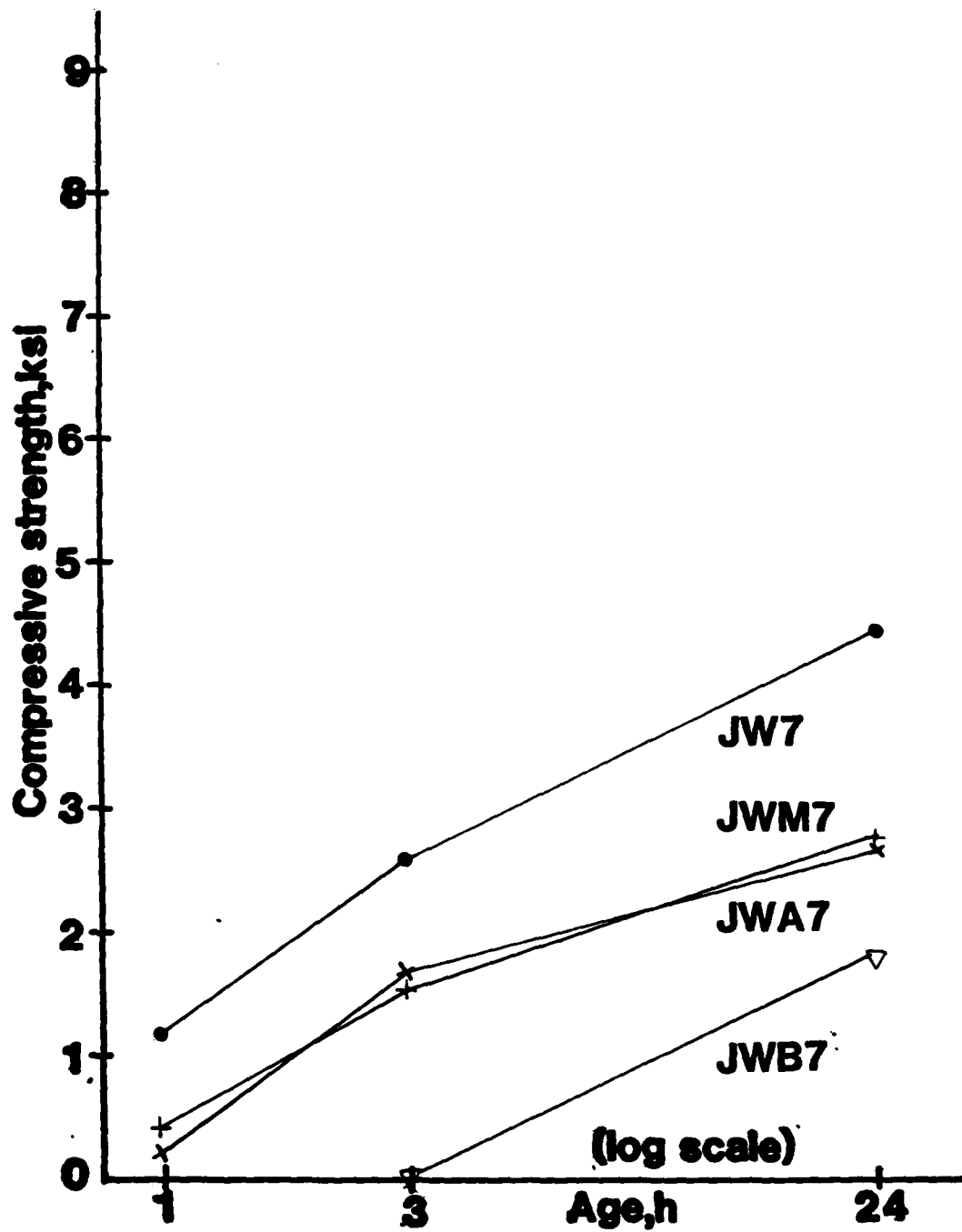


Fig. 14 - Relationship between compressive strength and early age of Jet cement

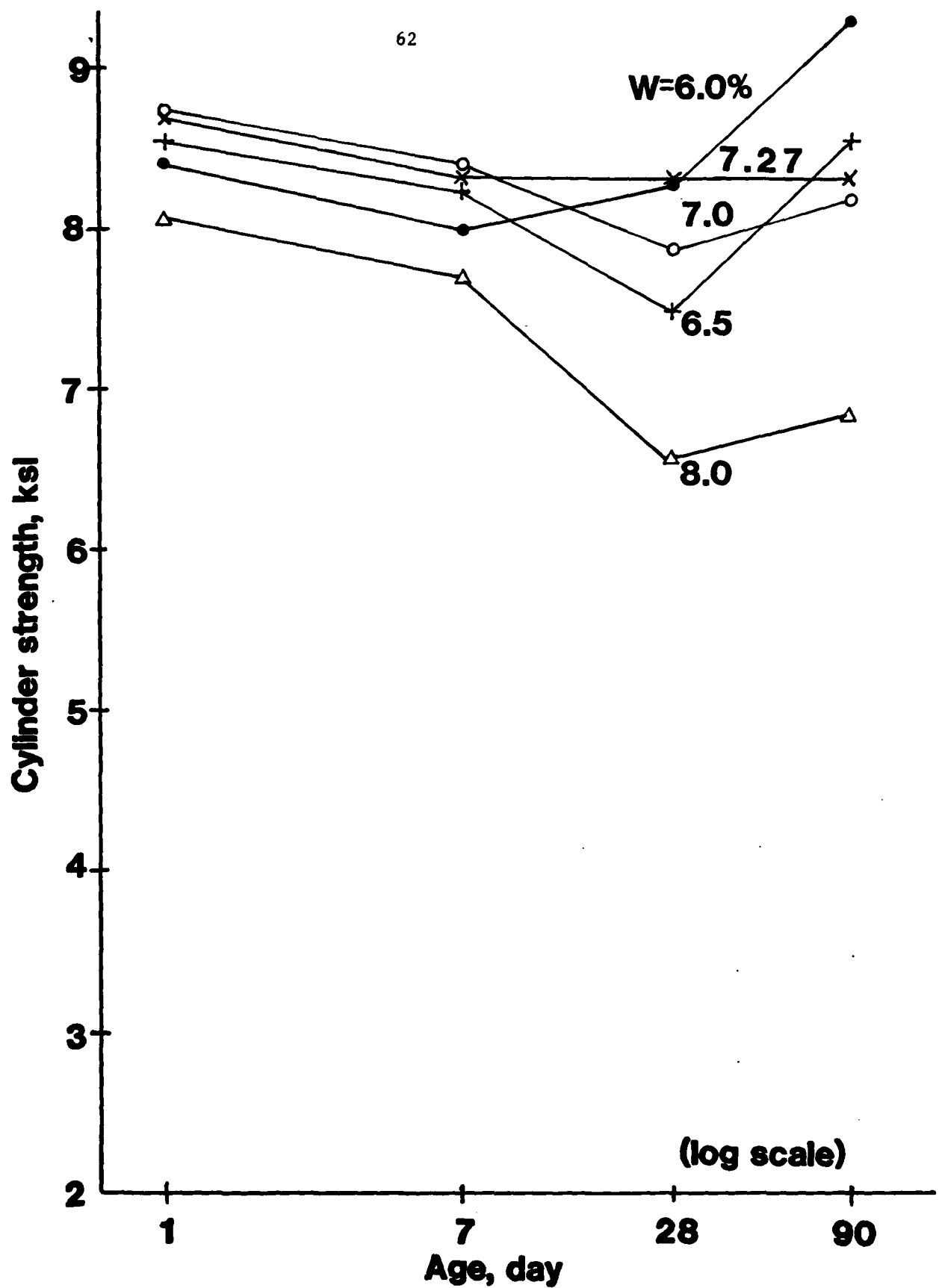


Fig. 15 - Relationship between cylinder strength and age of SET-45 cold mortars for various water contents (6 to 8.0%)

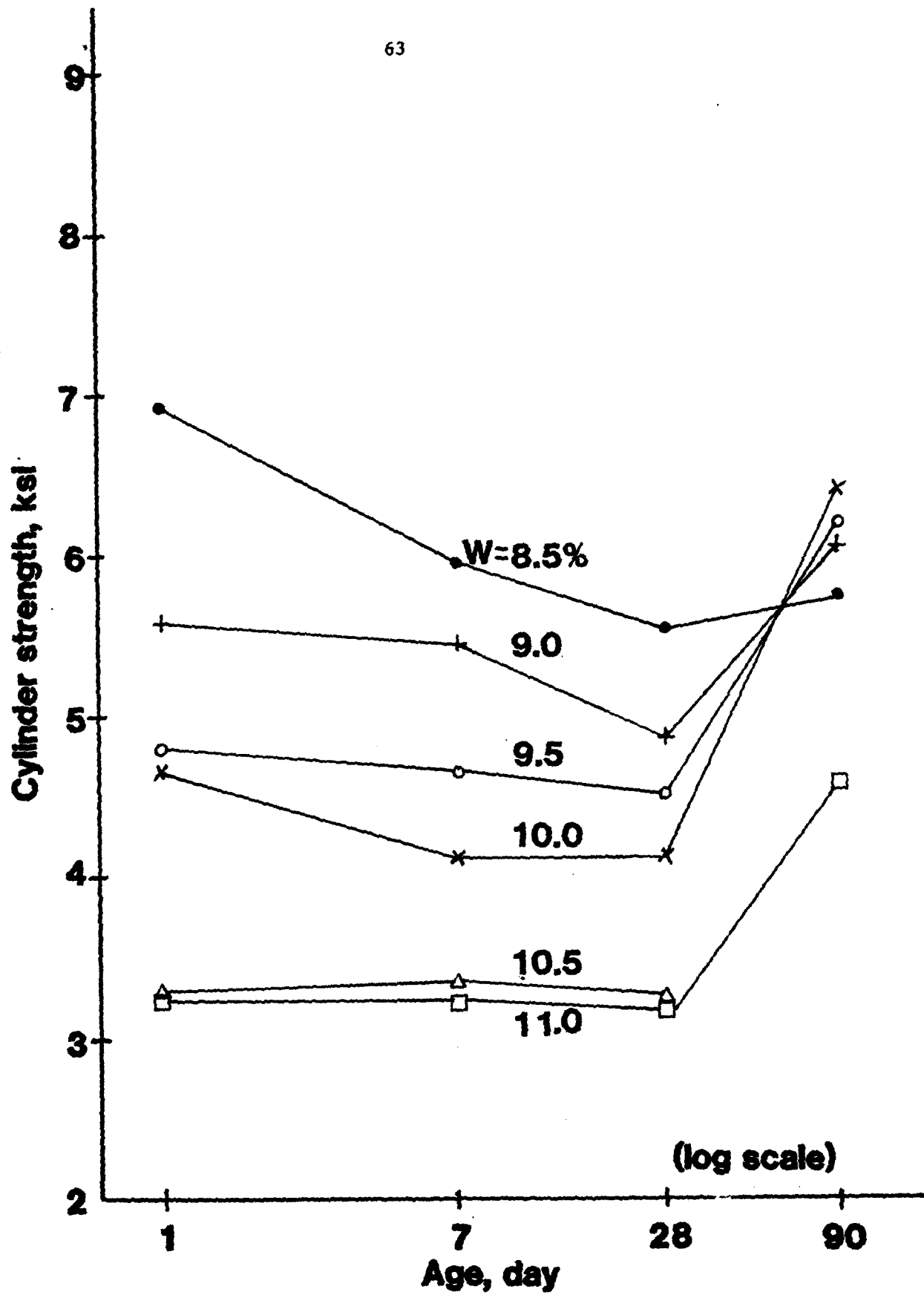


Fig. 16 ~ Relationship between cylinder strength and age of SET-45 cold mortars for various water contents (8.5 to 11.0%)

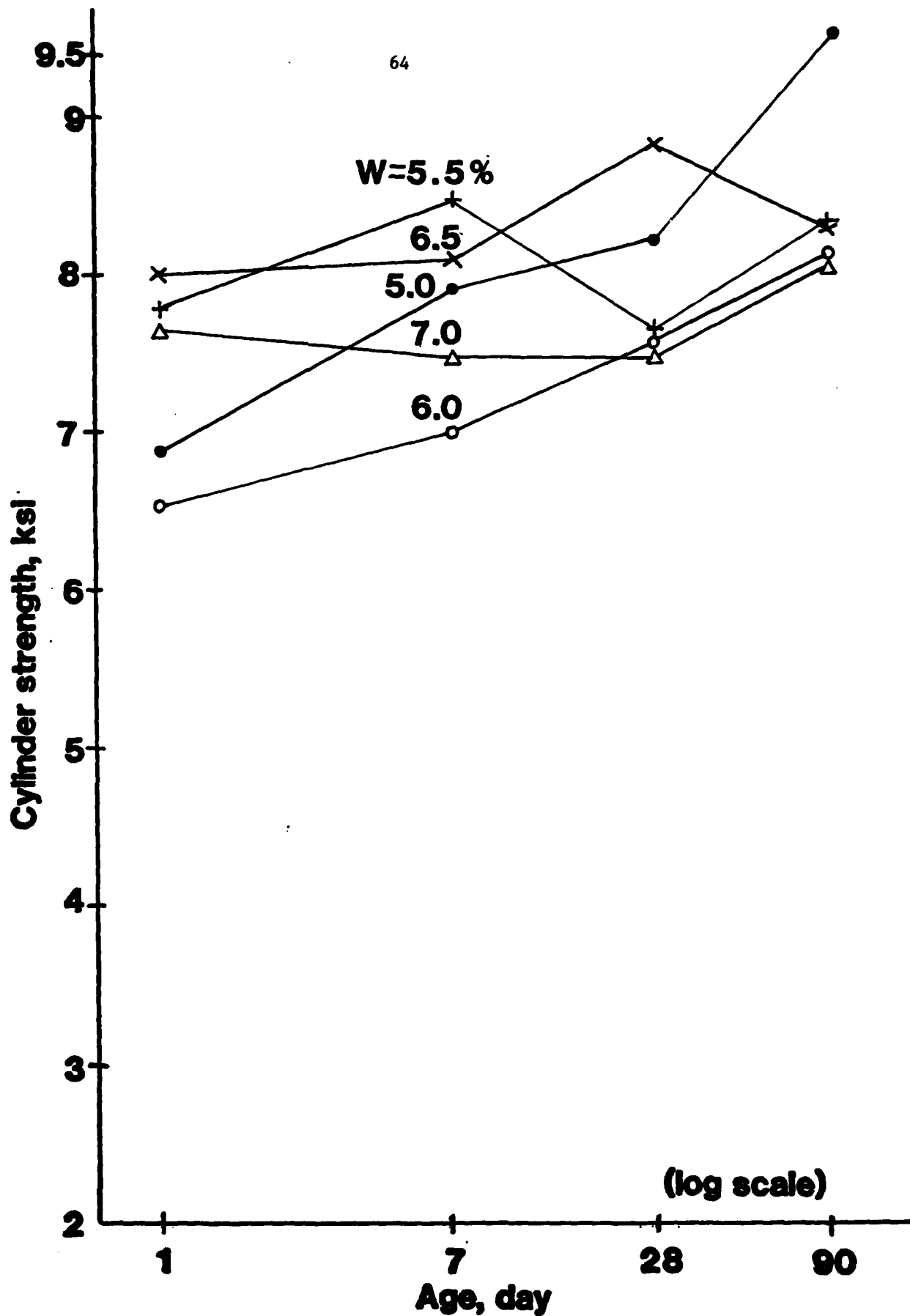


Fig. 17 - Relationship between cylinder strength and age of SET-45 hot mortars for various water contents (5.0 to 7.0%)

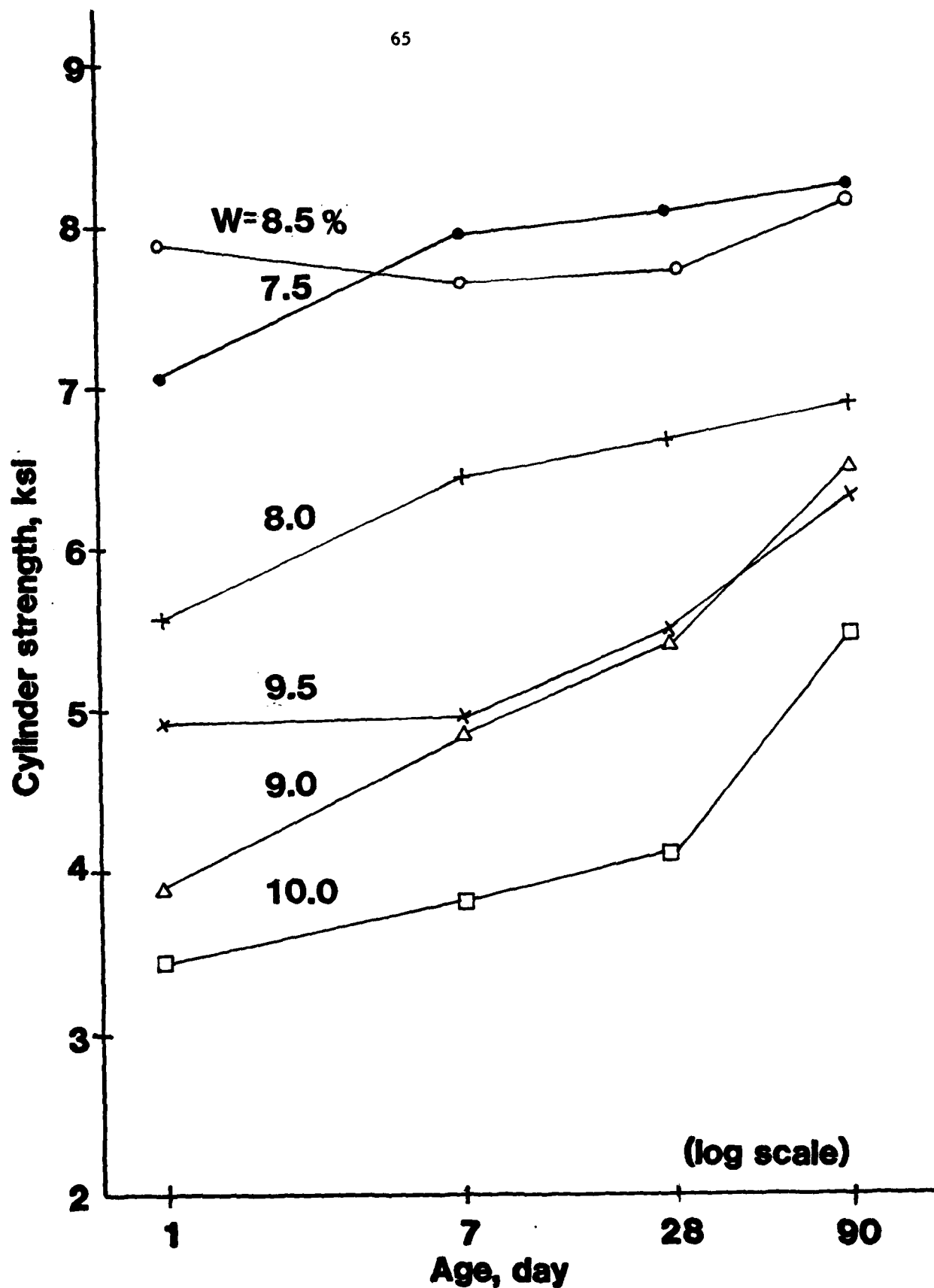


Fig. 18 - Relationship between cylinder strength and age of SET-45 hot mortars for various water contents (7.5 to 10.0%)

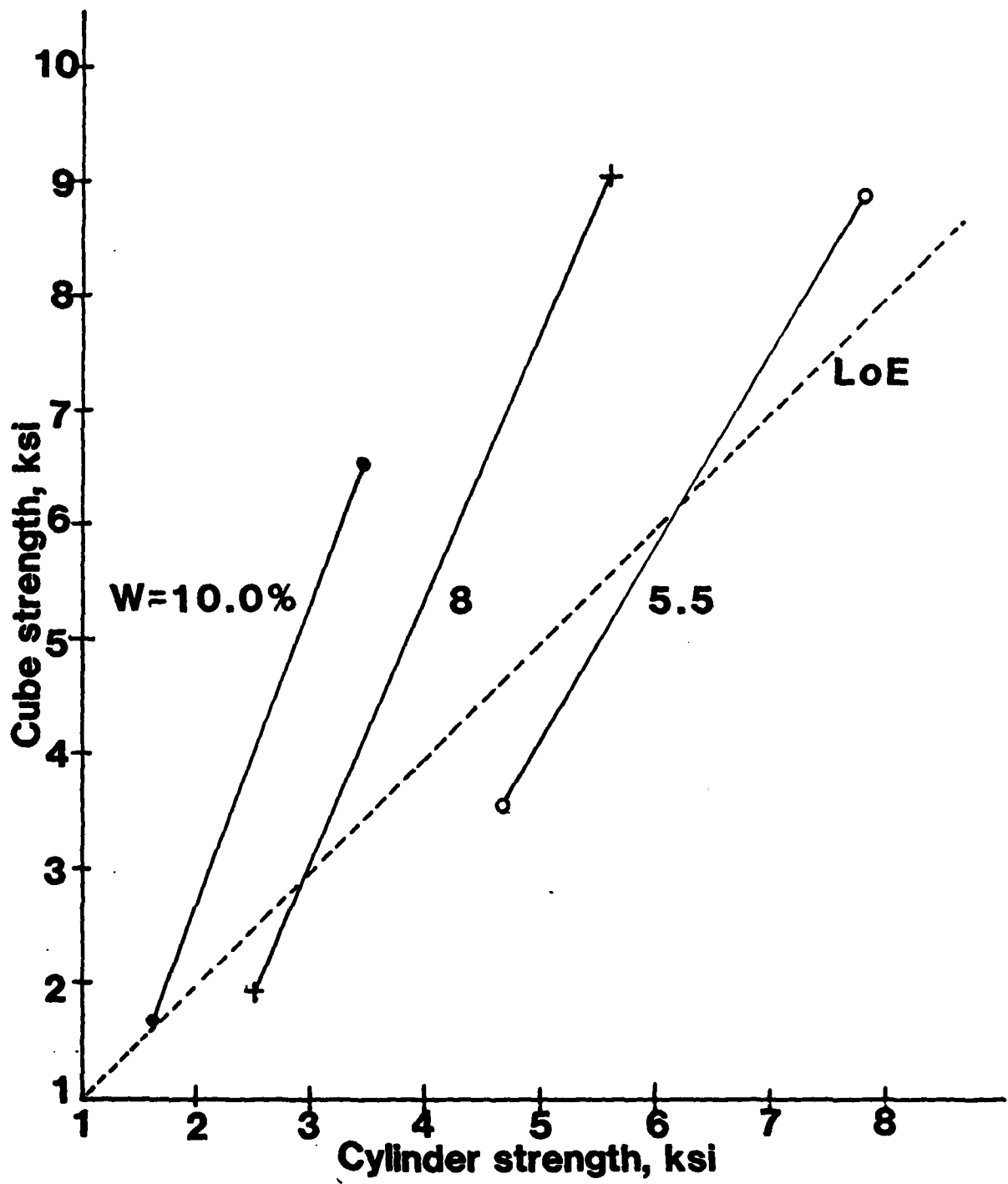


Fig. 19 - Relationship between cube and cylinder strengths of SET-45
hot mortars with various water contents and ages

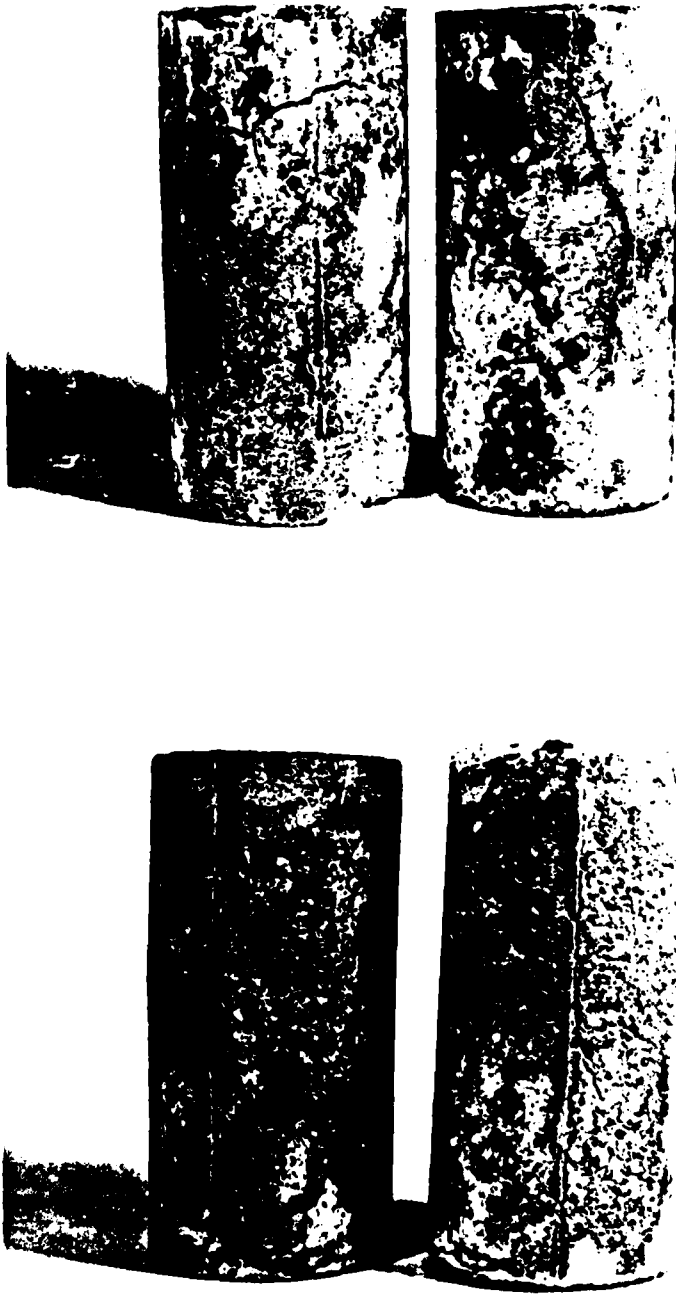


Fig. 20. Cracked specimens made with SET-45 cold mortar and 10.5 % water after 28 days of curing in fog room.

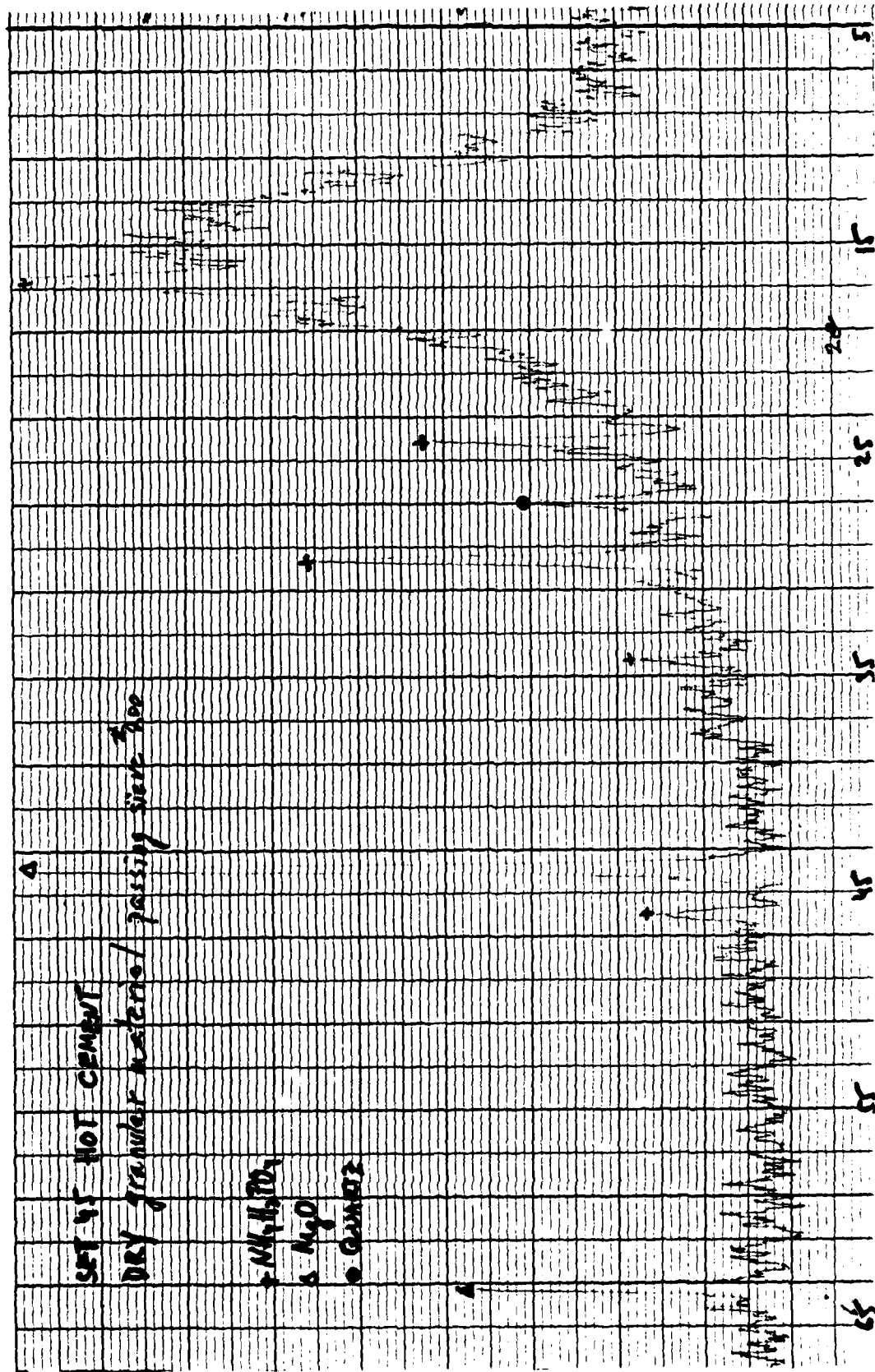


Fig. 21 - X-ray diffraction pattern of SET-45 hot weather mixture passing sieve no. 200.

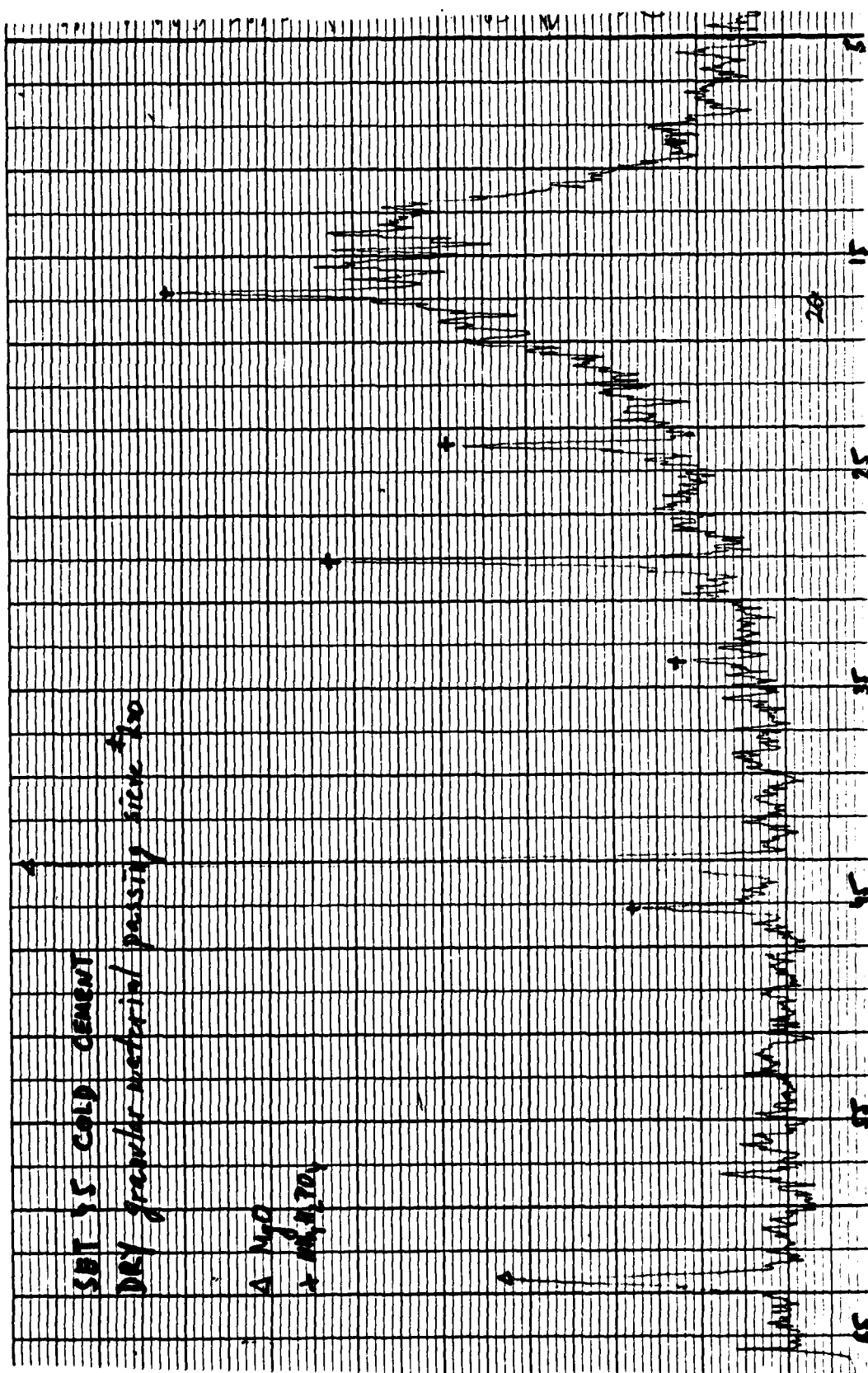


Fig. 22 - X-ray diffraction pattern of SET-45 cold weather mixture passing sieve no. 200.

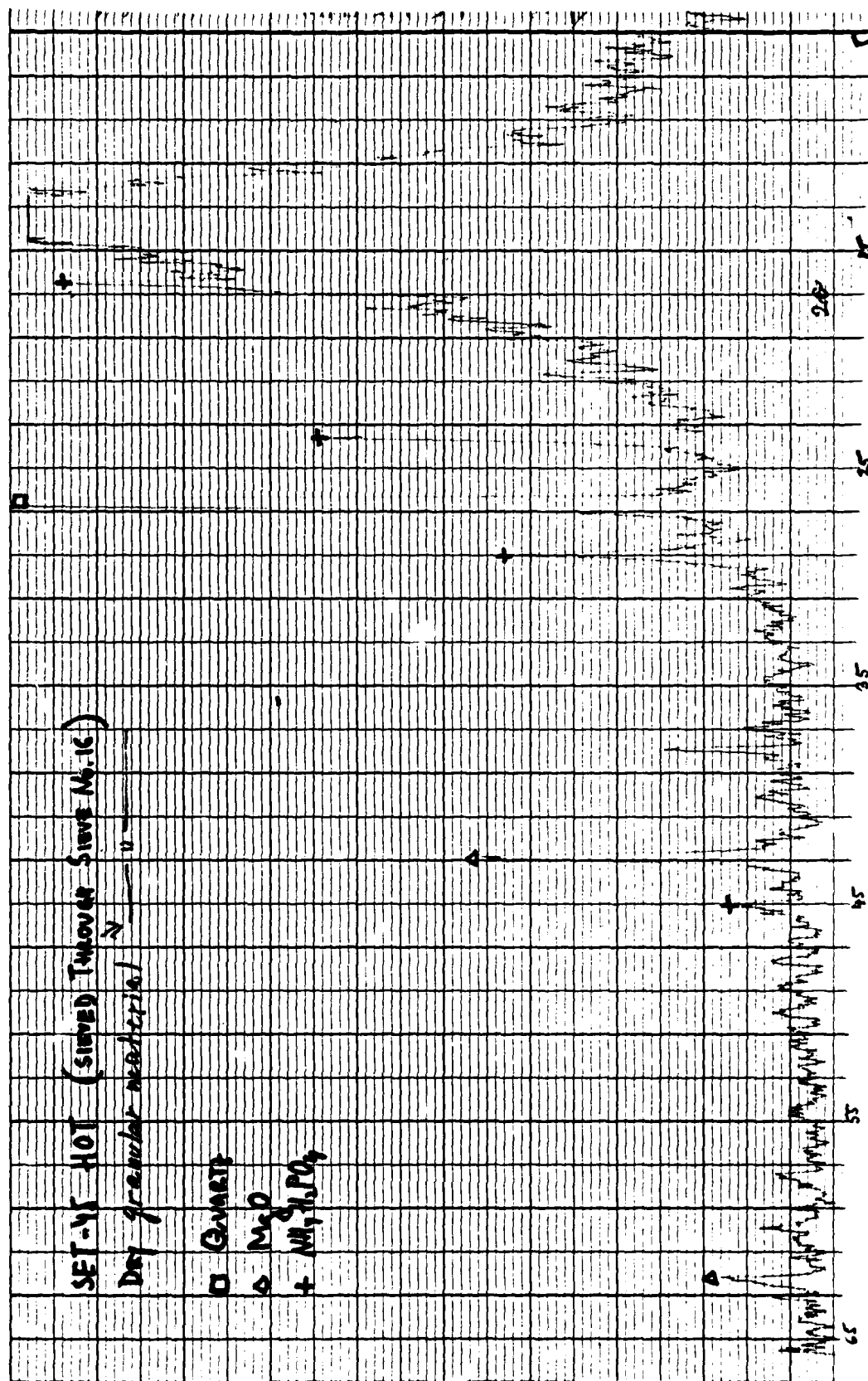


Fig. 23 - X-ray diffraction pattern of SET-45 hot weather mixture passing sieve no. 16.

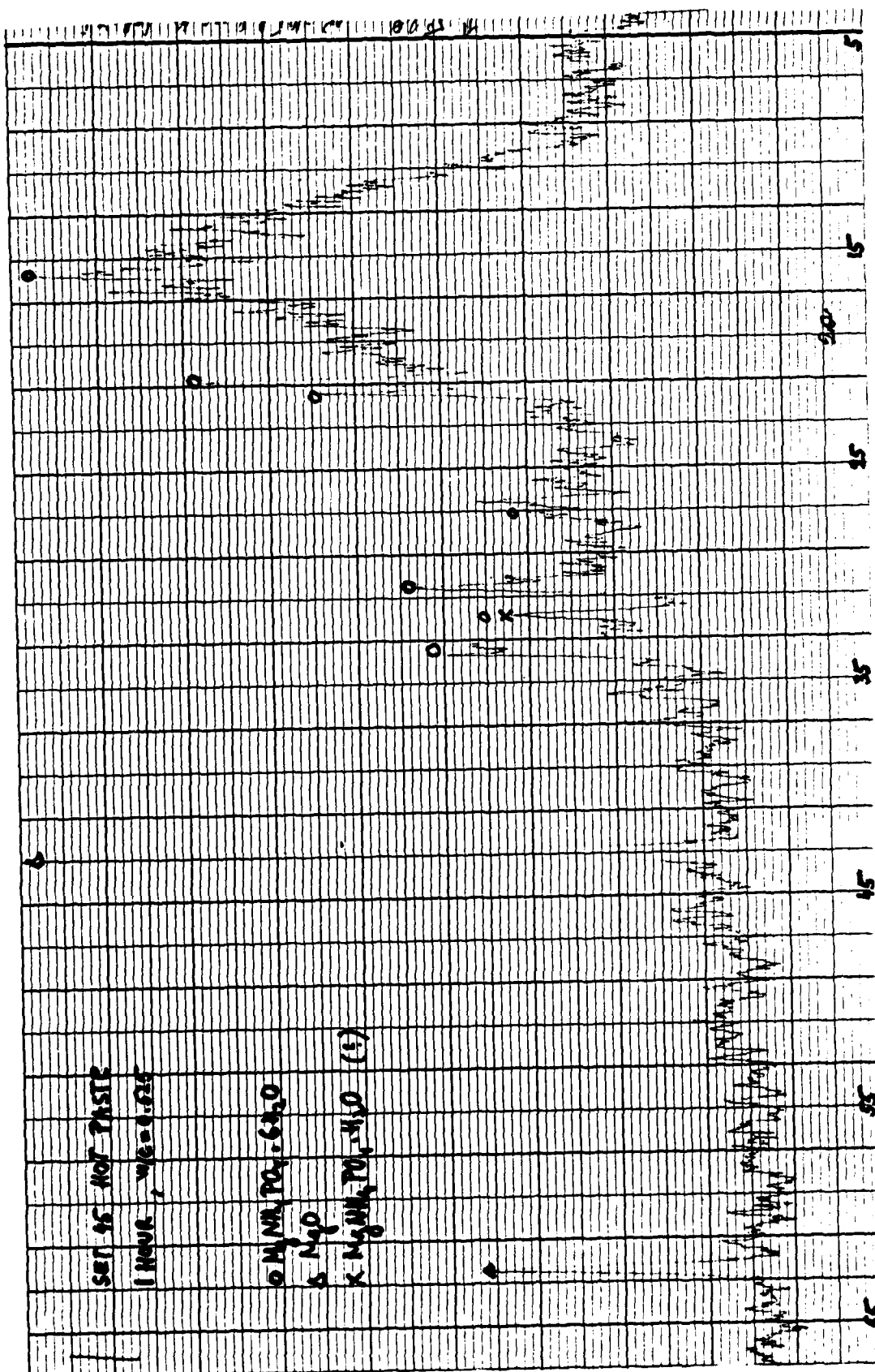


Fig. 24 - X-ray diffraction pattern of SET-45 hot weather paste of high water content at 1 hour.

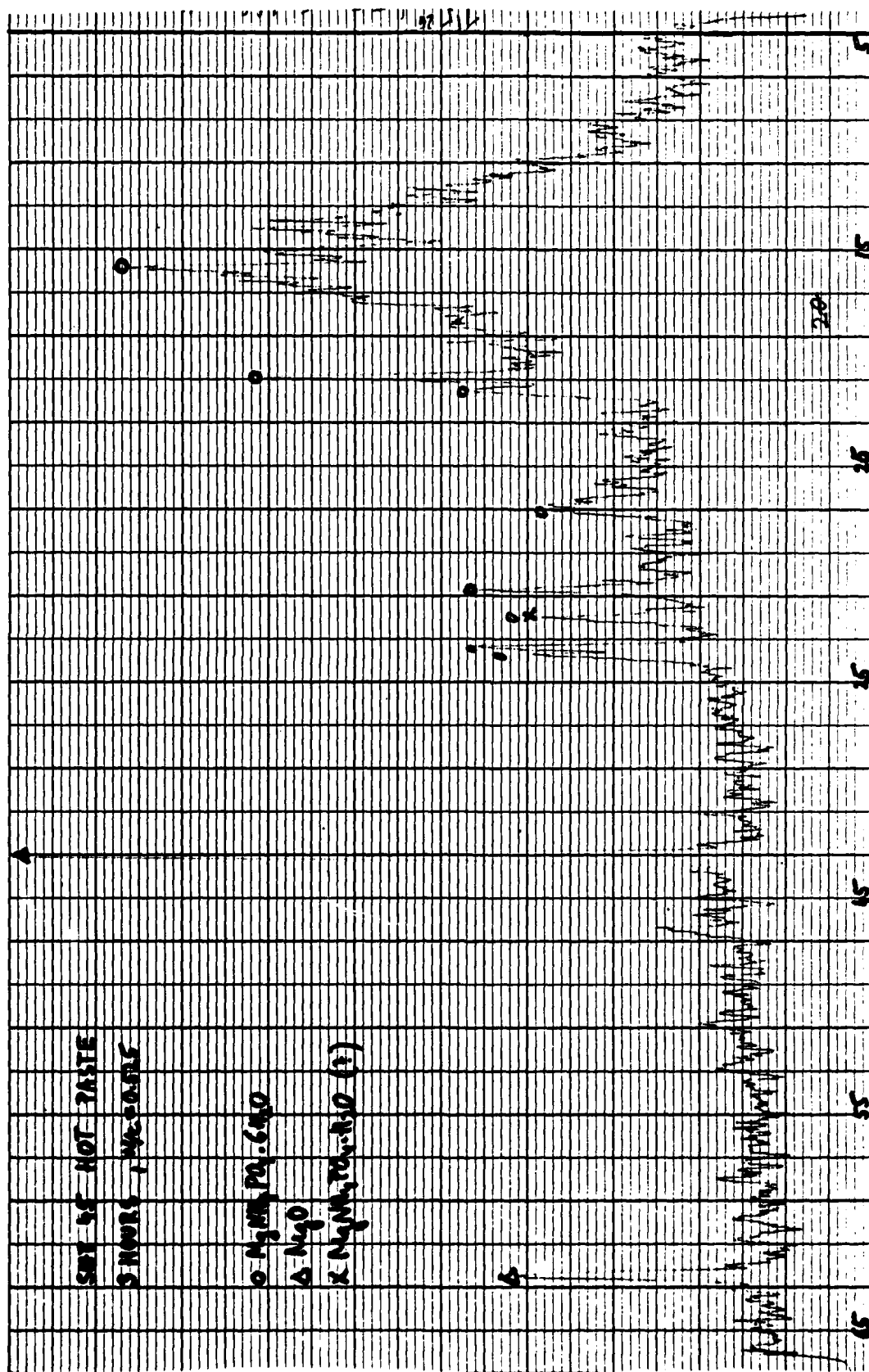


Fig. 25 - X-ray diffraction pattern of SER-45 hot weather paste of high water content at 3 hours.

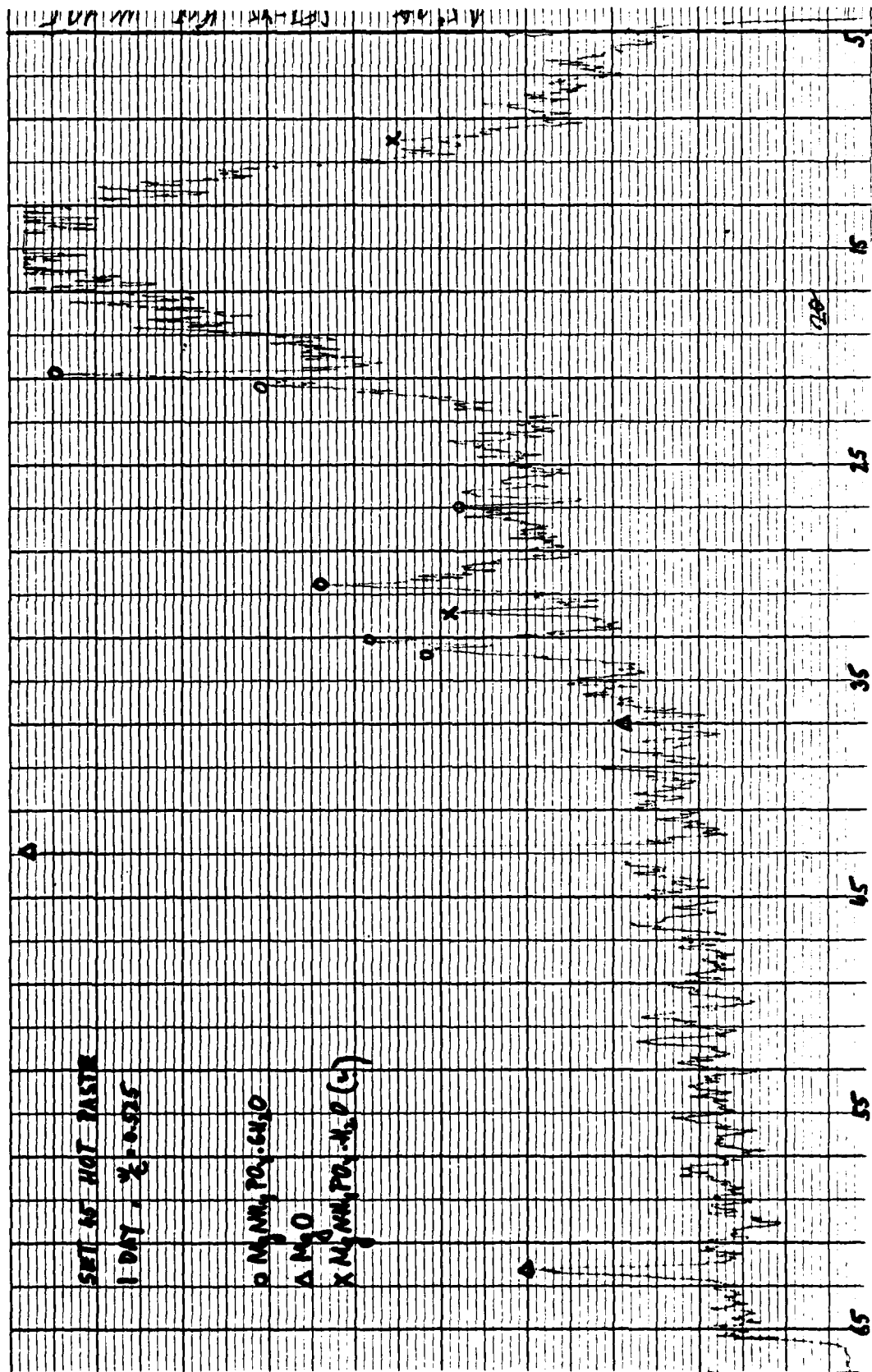


Fig. 26 - X-ray diffraction pattern of SET-45 hot weather paste of high water content at 1 day.

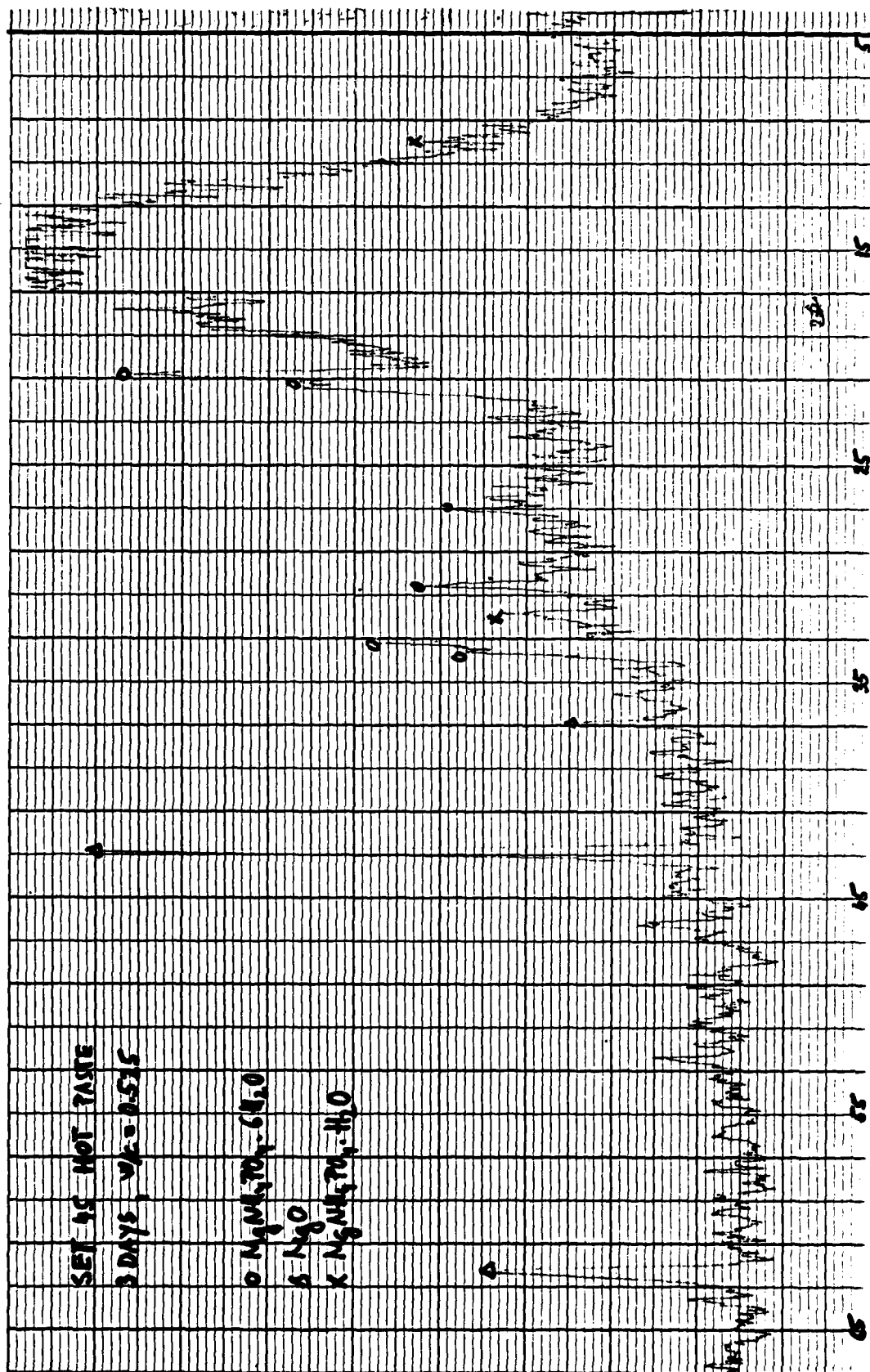


Fig. 27 - X-ray diffraction pattern of SET-45 hot weather paste of high water content at 3 days.

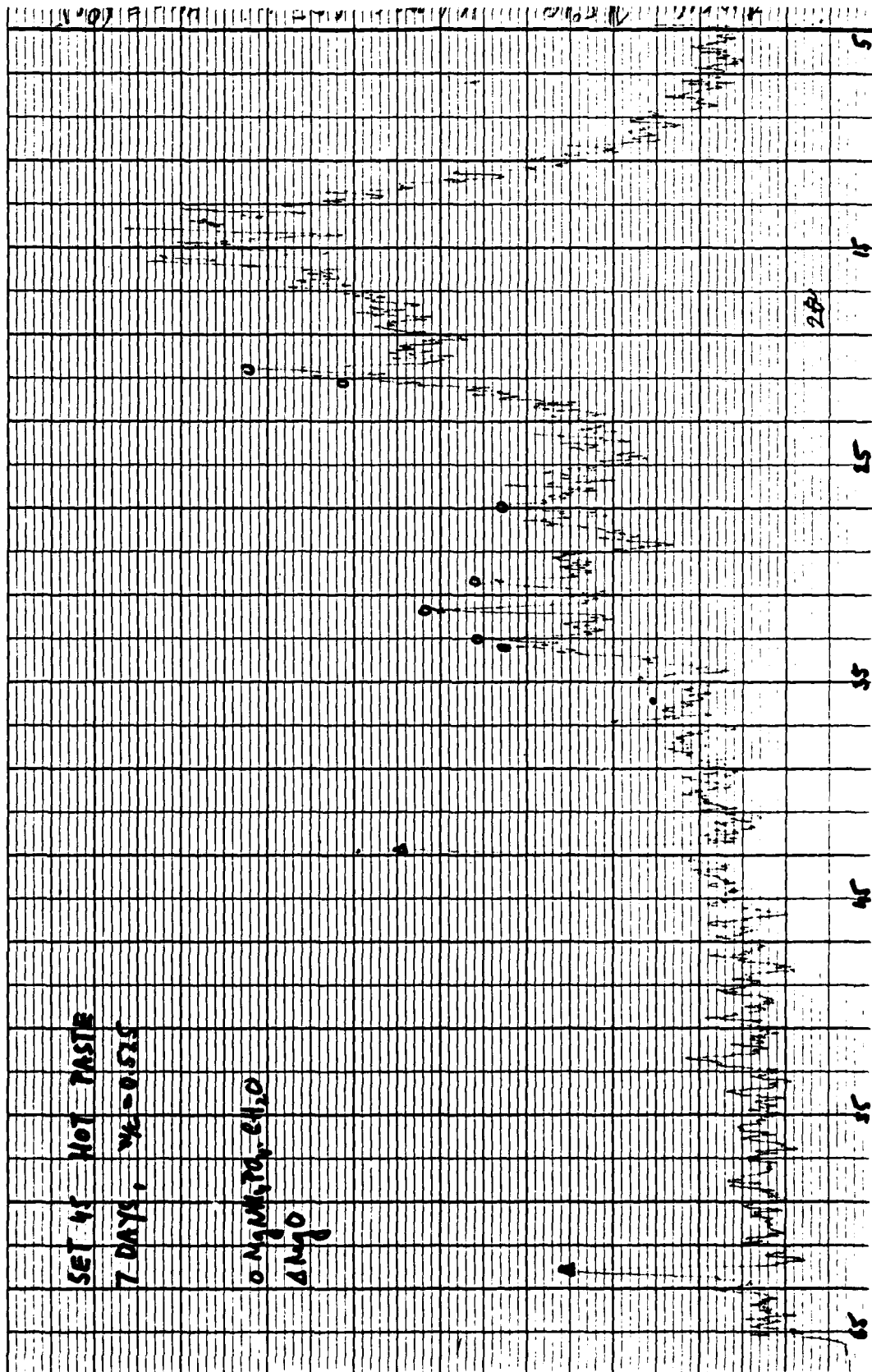


Fig. 28 - X-ray diffraction pattern of SET-45 hot weather paste of high water content at 7 days.

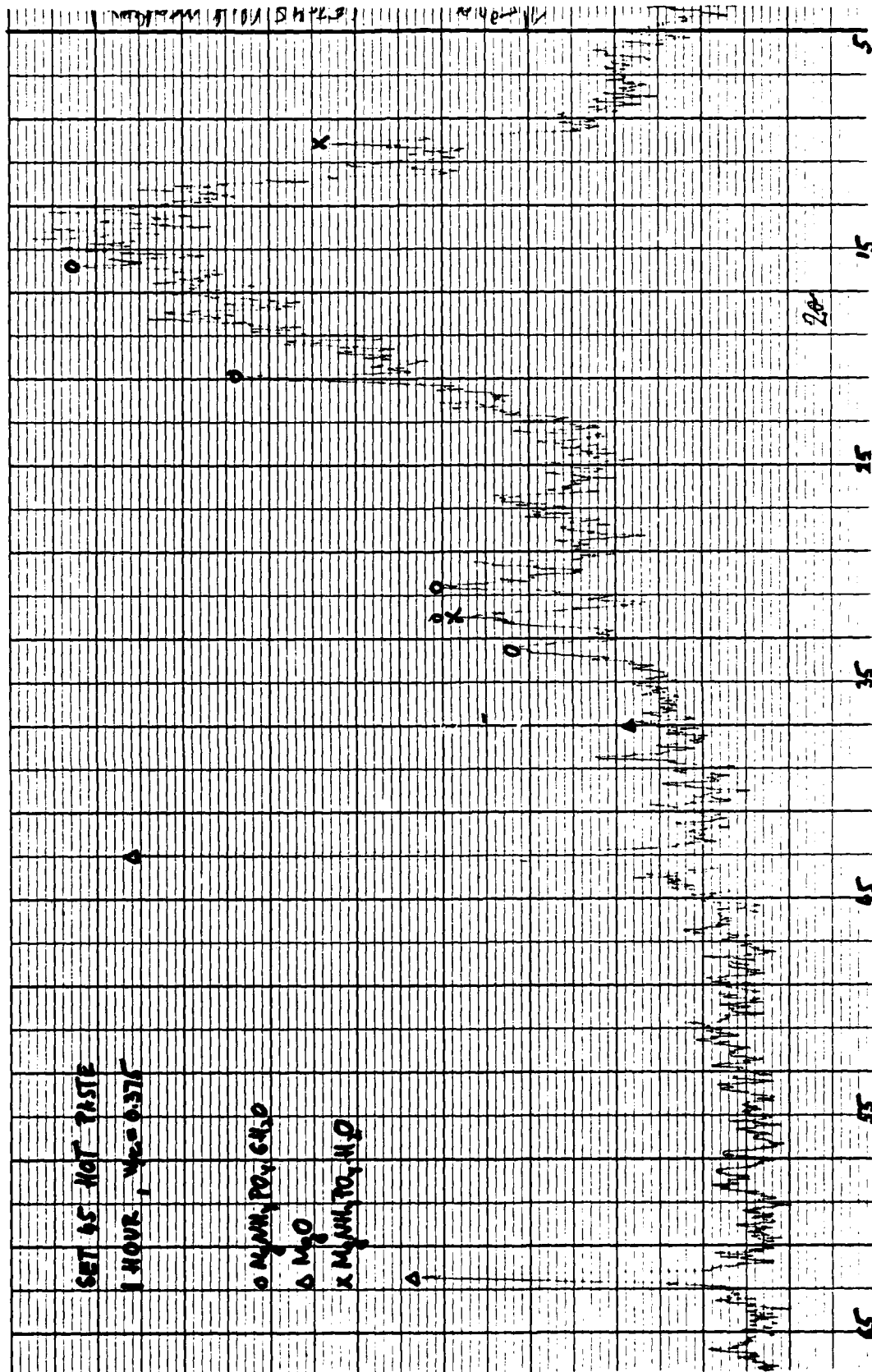


Fig. 29 - X-ray diffraction pattern of SET-45 hot weather paste of low water content at 1 hour.

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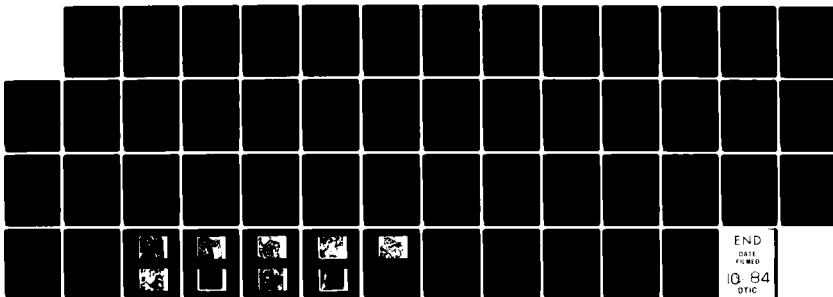
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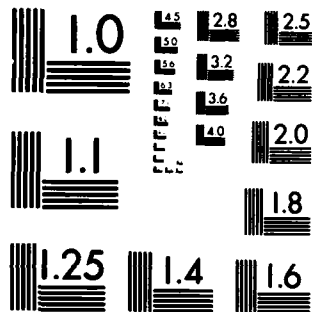
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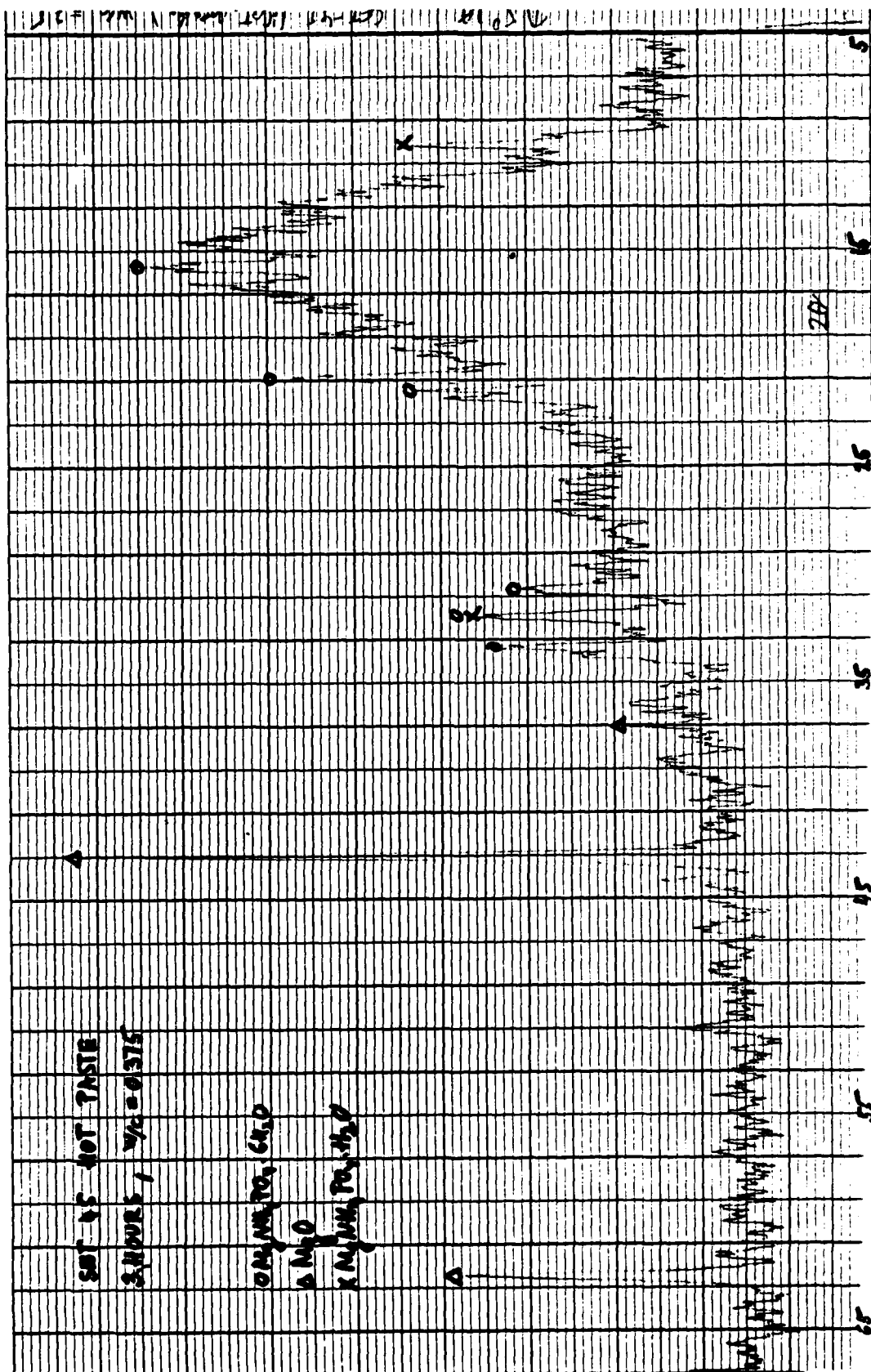


Fig. 30 - X-ray diffraction pattern of SET-45 hot weather paste of low water content at 3 hours.

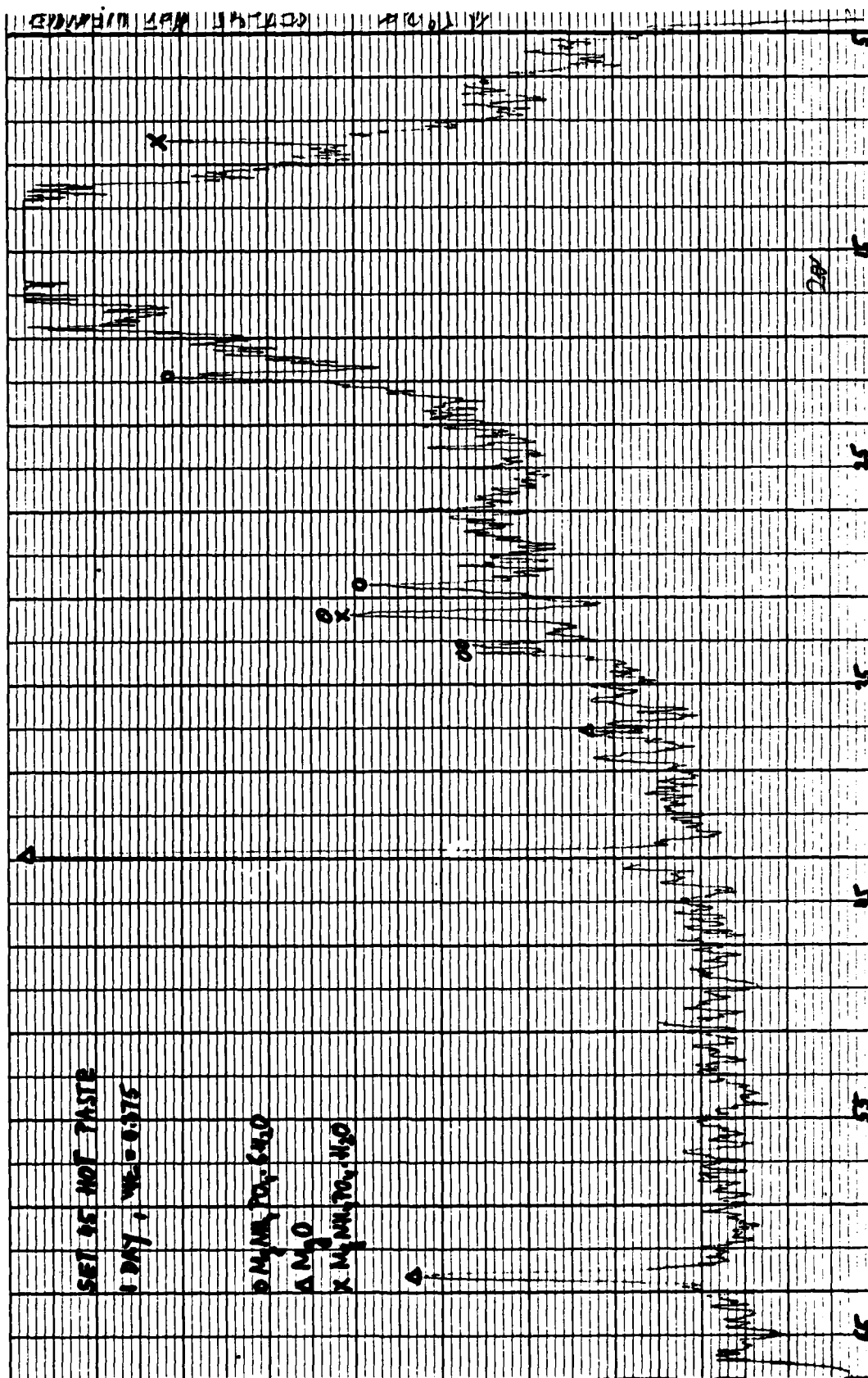


Fig. 31 - X-ray diffraction pattern of SET-45 hot weather paste of low water content at 1 day.

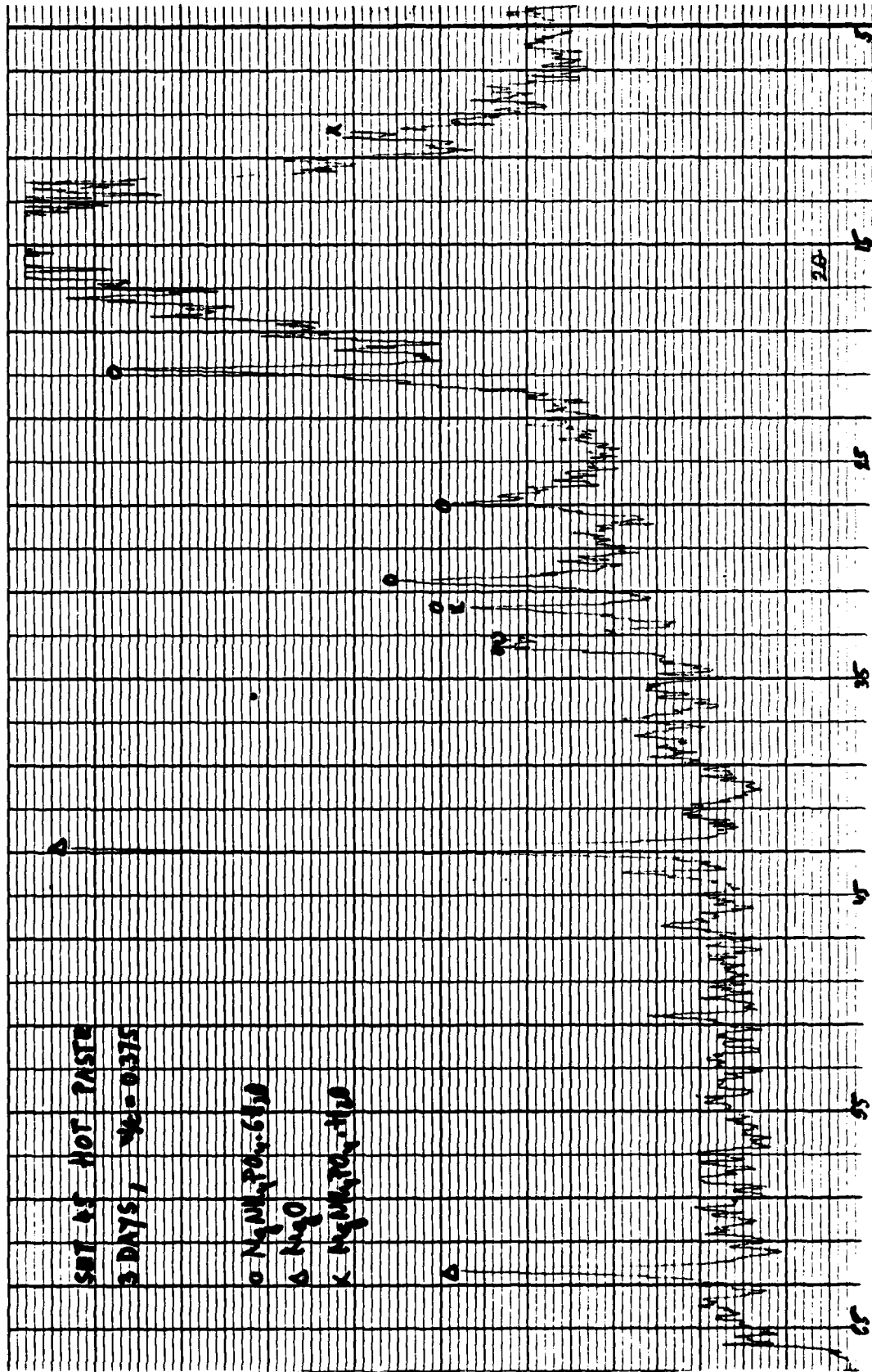


Fig. 32 - X-ray diffraction pattern of SET-45 hot weather paste of low water content at 3 days.

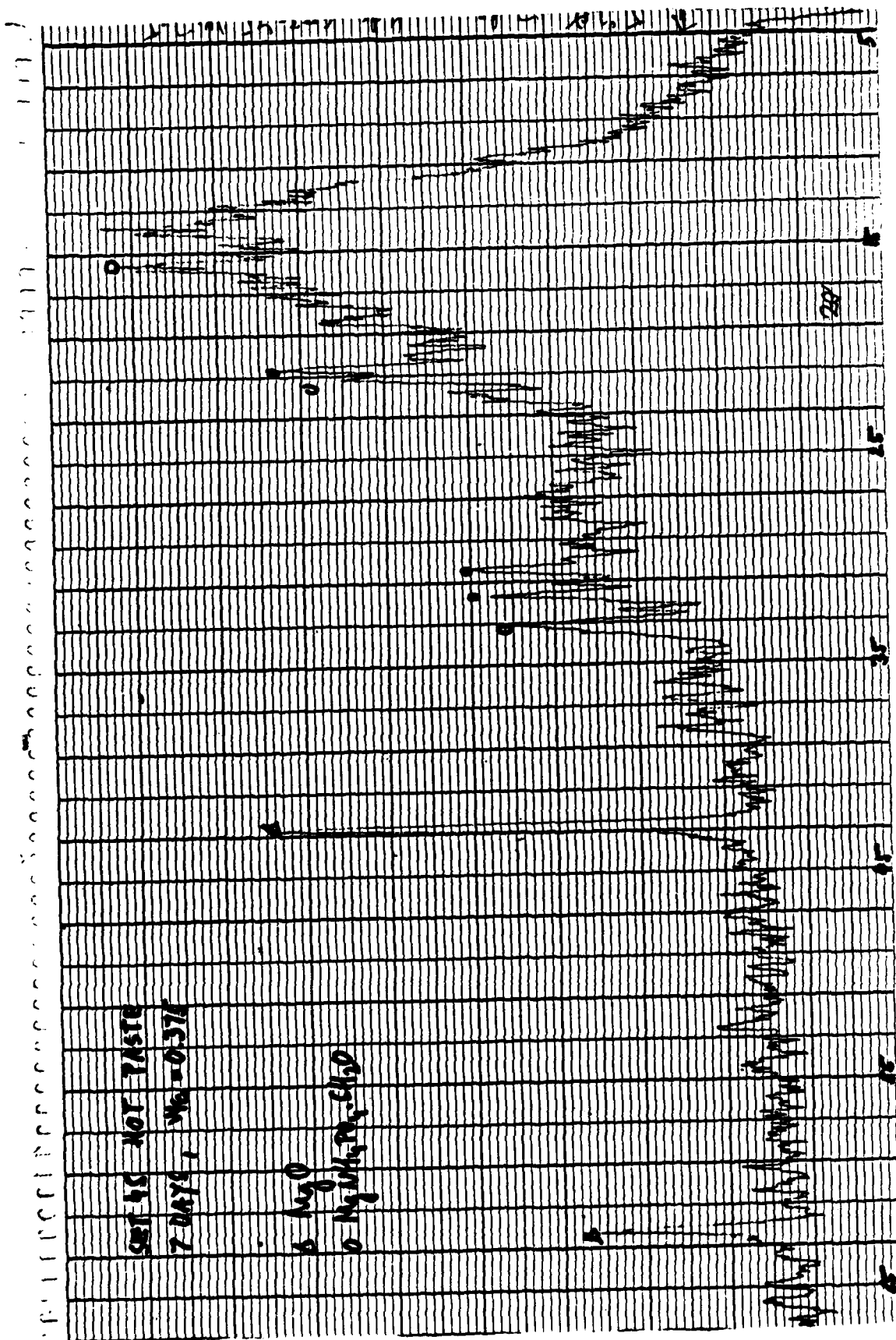


Fig. 33 - X-ray diffraction pattern of SET-45 hot weather paste of low water content at 7 days.

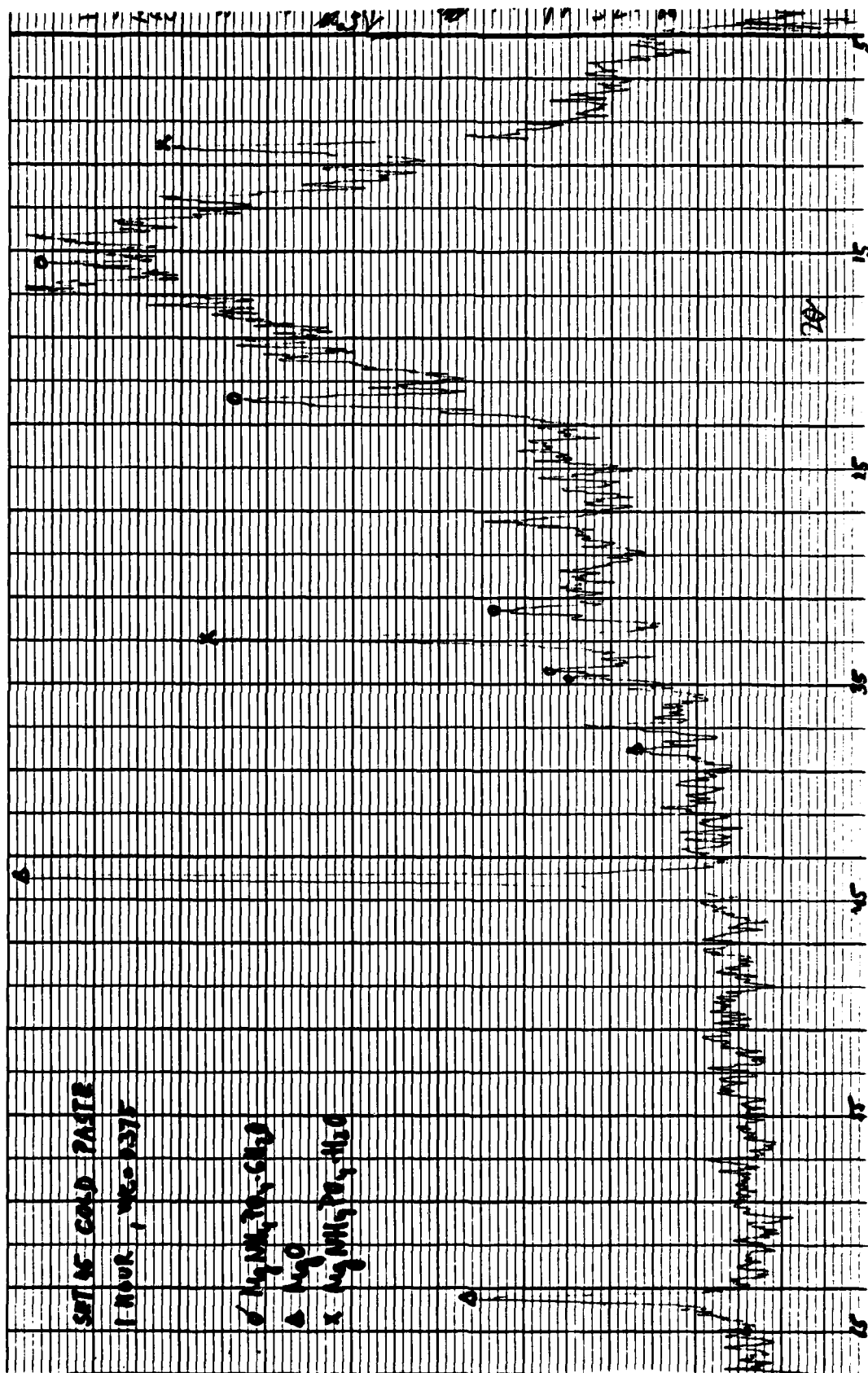


Fig. 34 - X-ray diffraction pattern of SET-45 cold weather paste of low water content at 1 hour.

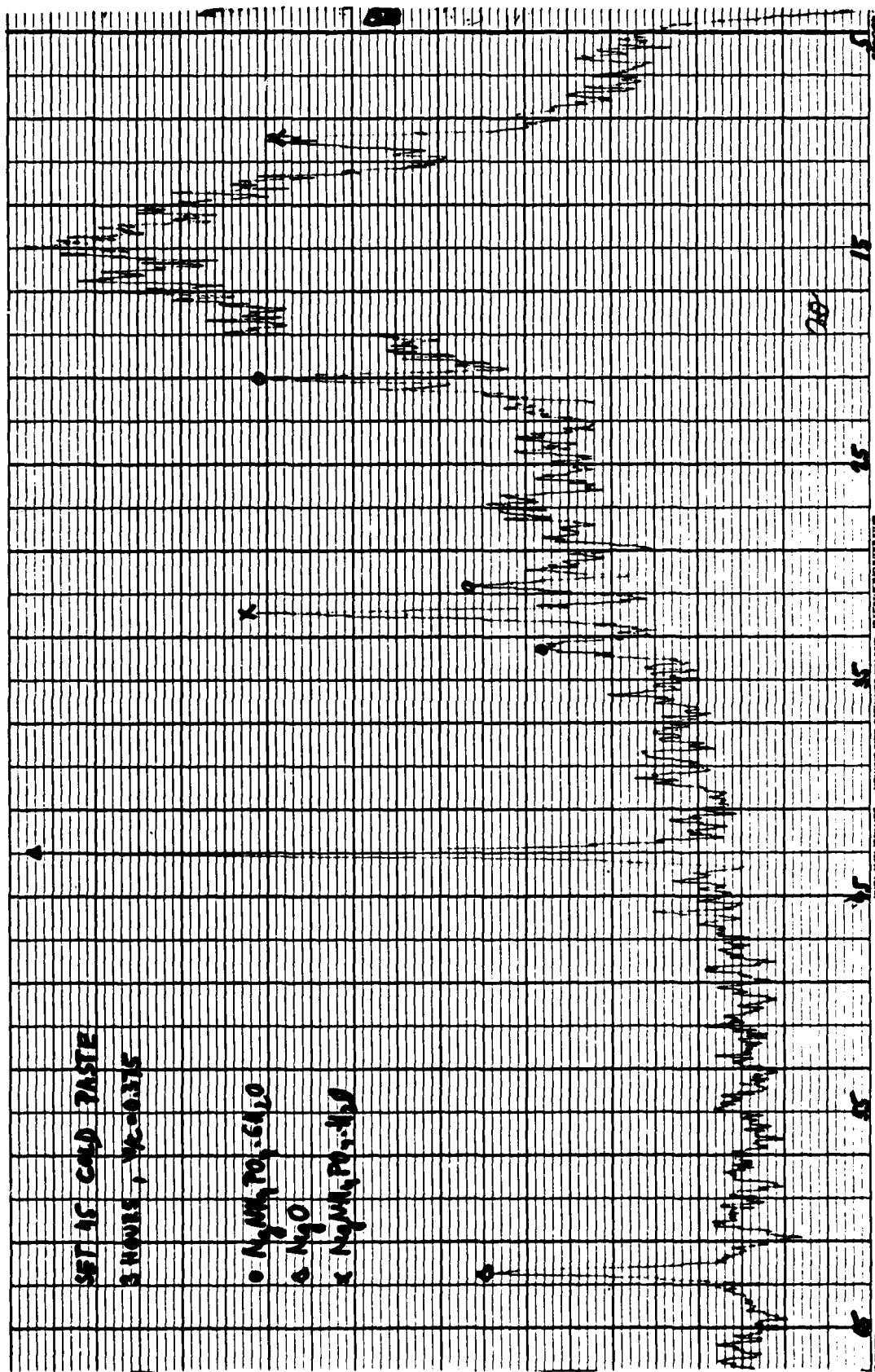


Fig. 35 - X-ray diffraction pattern of SET-45 cold weather paste of low water content at 3 hours.

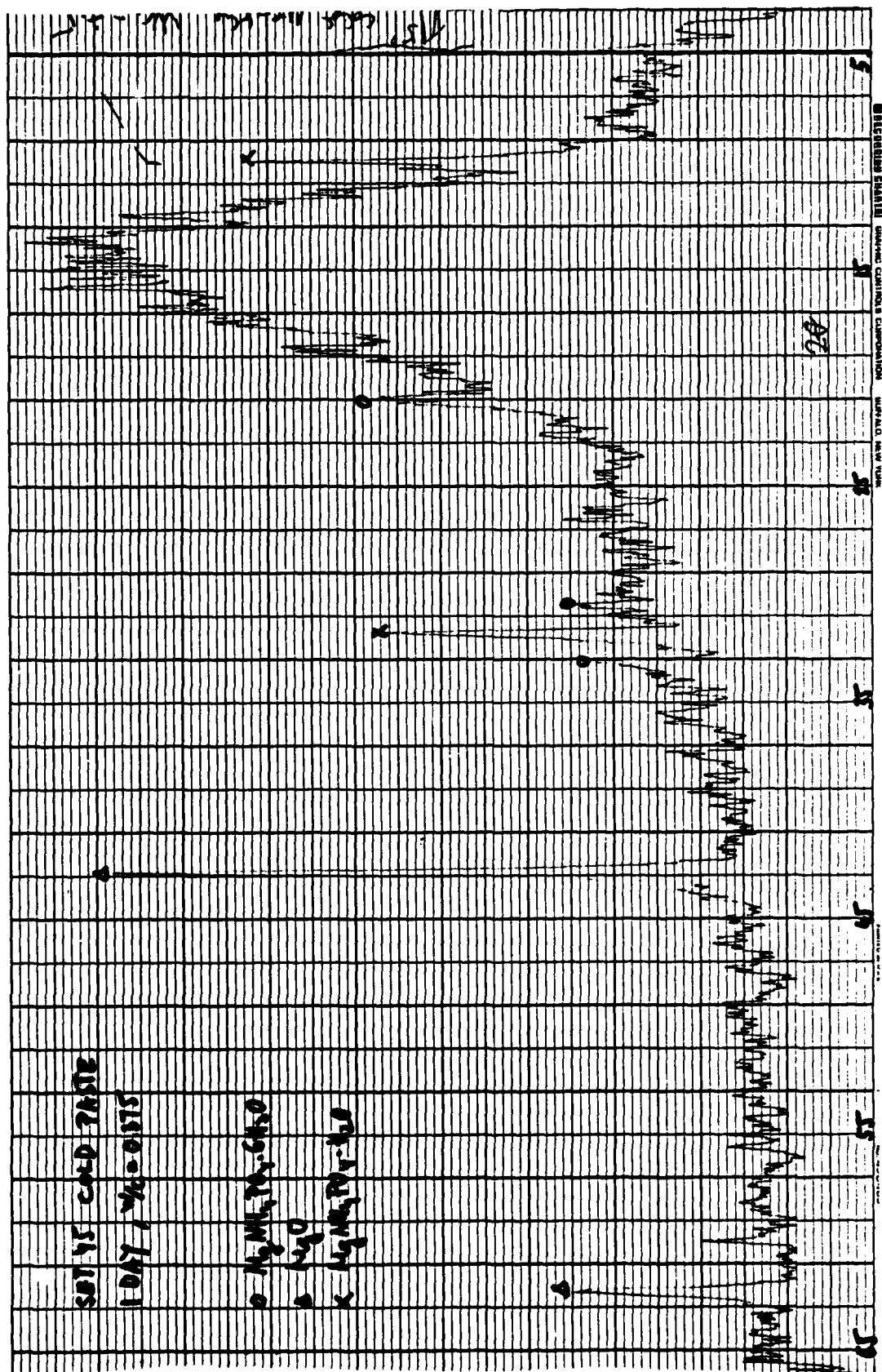


Fig. 36 - X-ray diffraction pattern of SET-45 cold weather paste of low water content at 1 day.

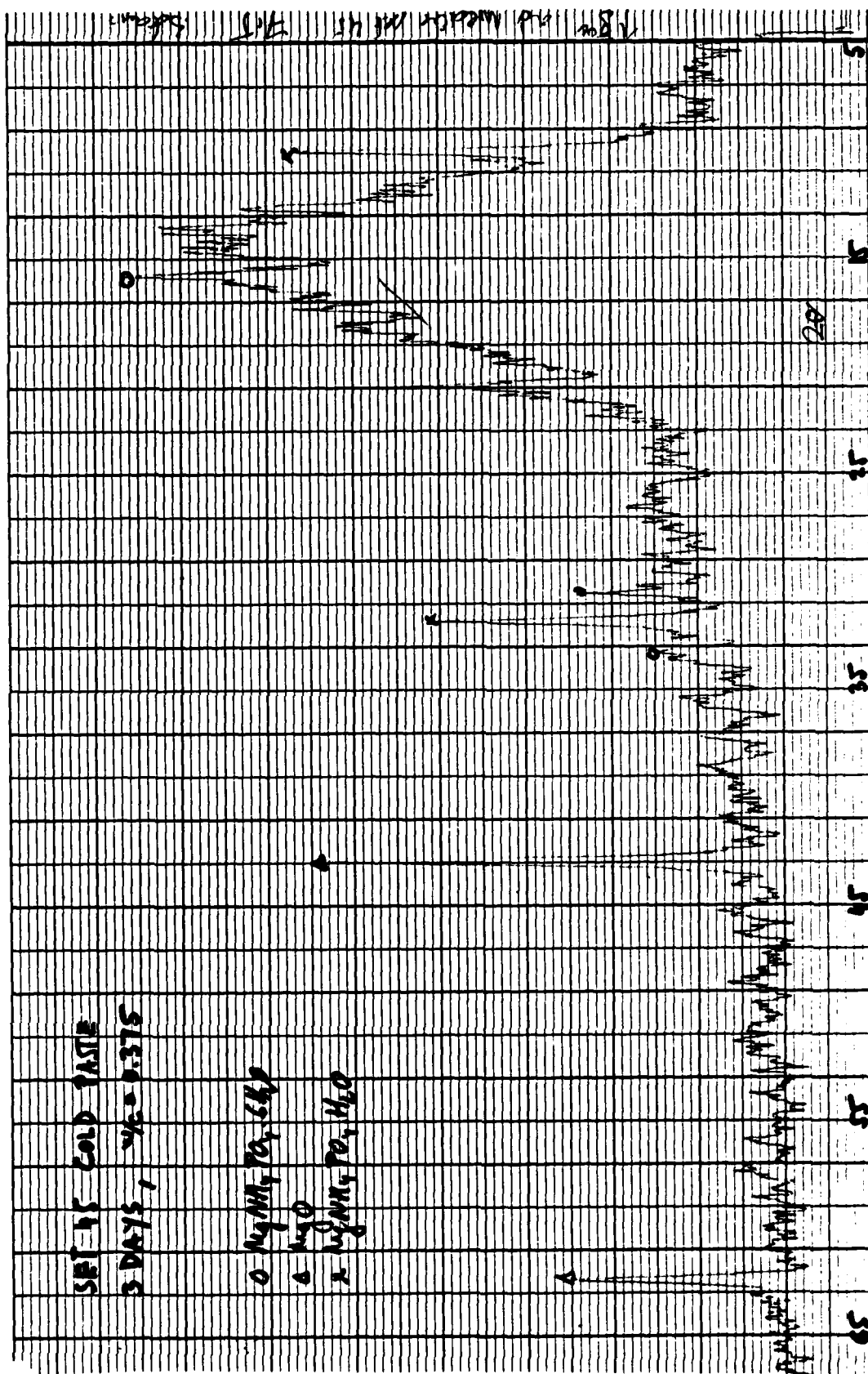


Fig. 37 - X-ray diffraction pattern of SET-45 cold weather paste of low water content at 3 days.

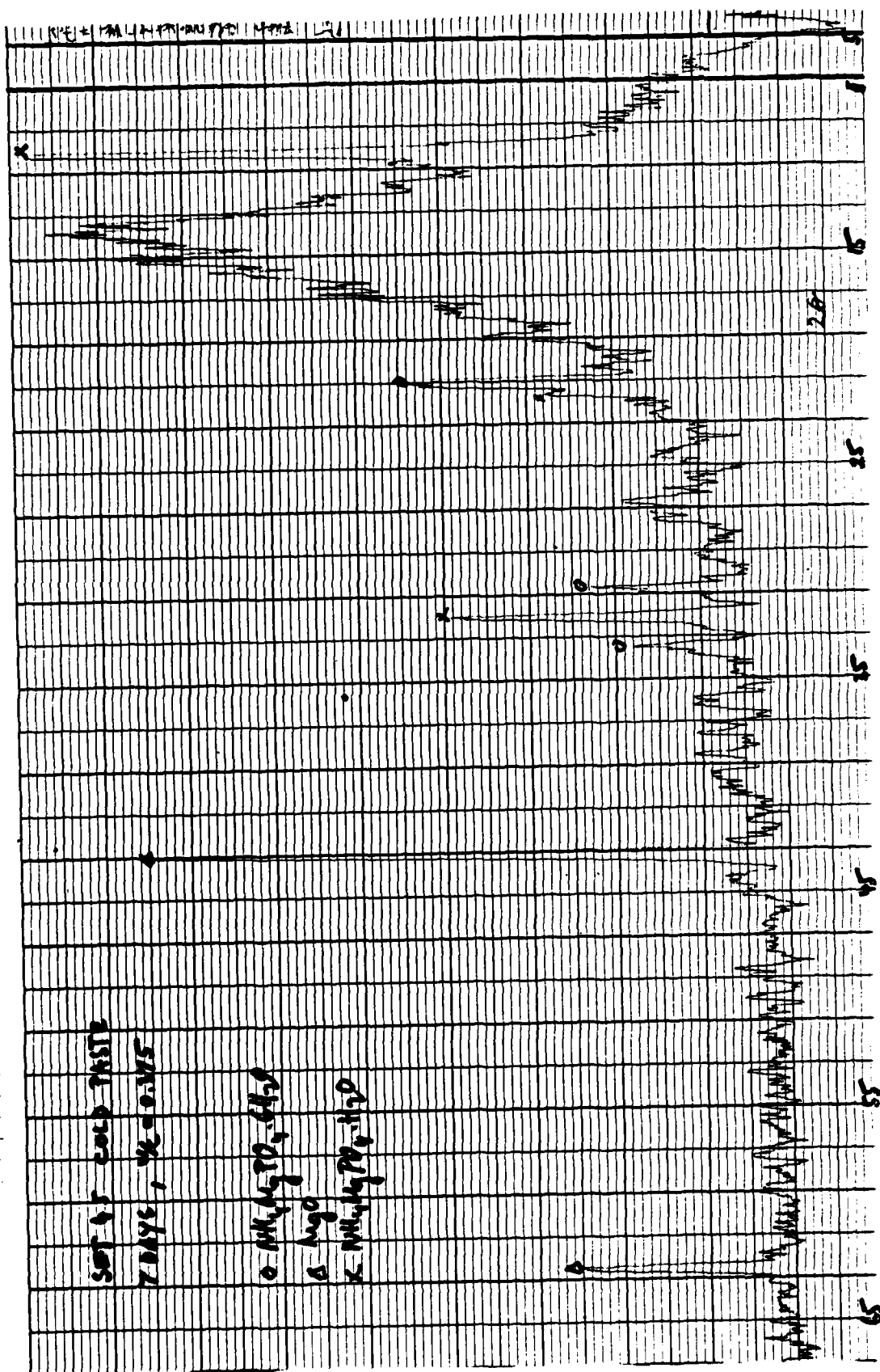


Fig. 38 - X-ray diffraction pattern of SET-45 cold weather paste of low water content at 7 days.

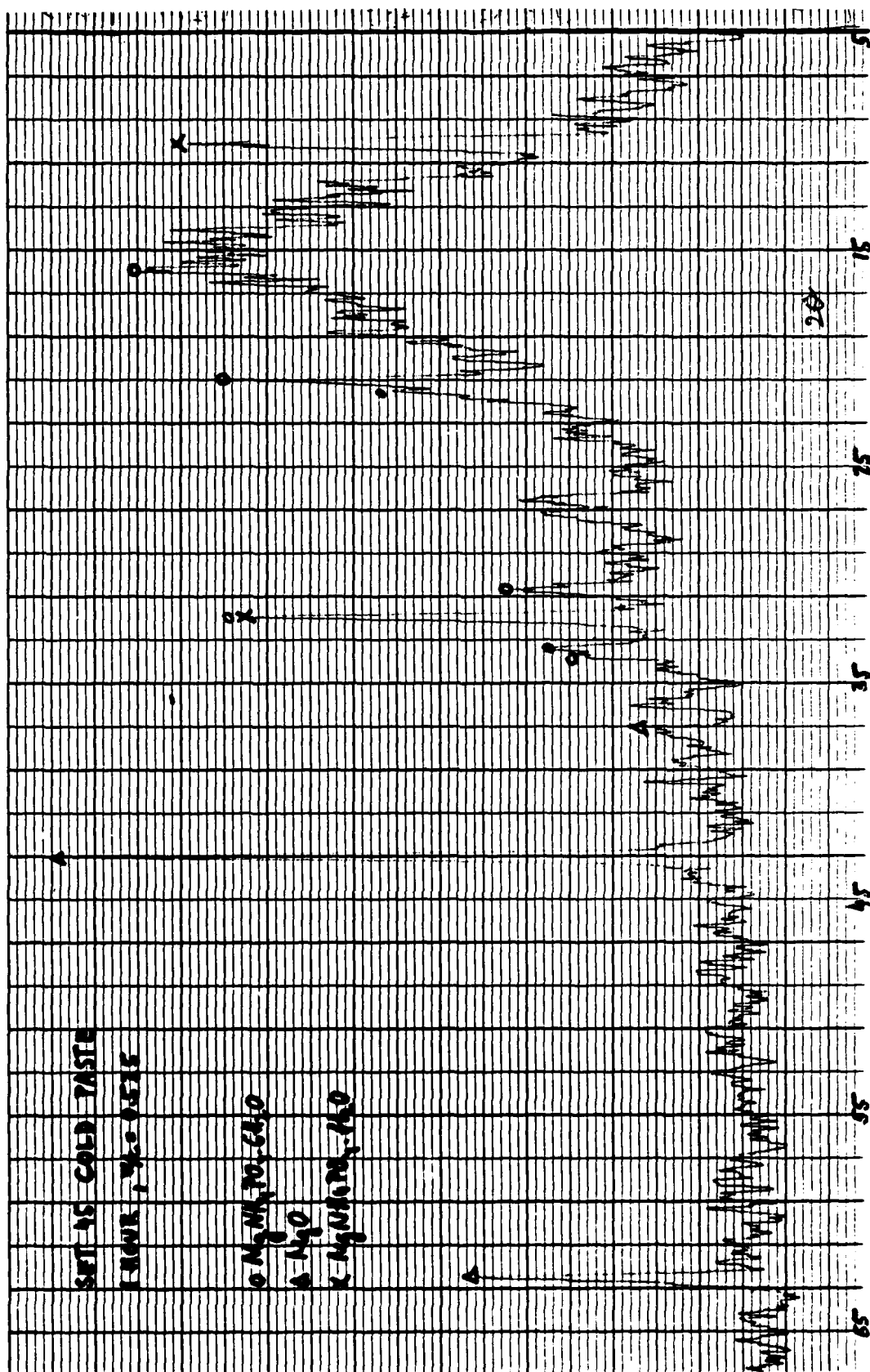


Fig. 39 - X-ray diffraction pattern of SET-45 cold weather paste of high water content at 1 hour.

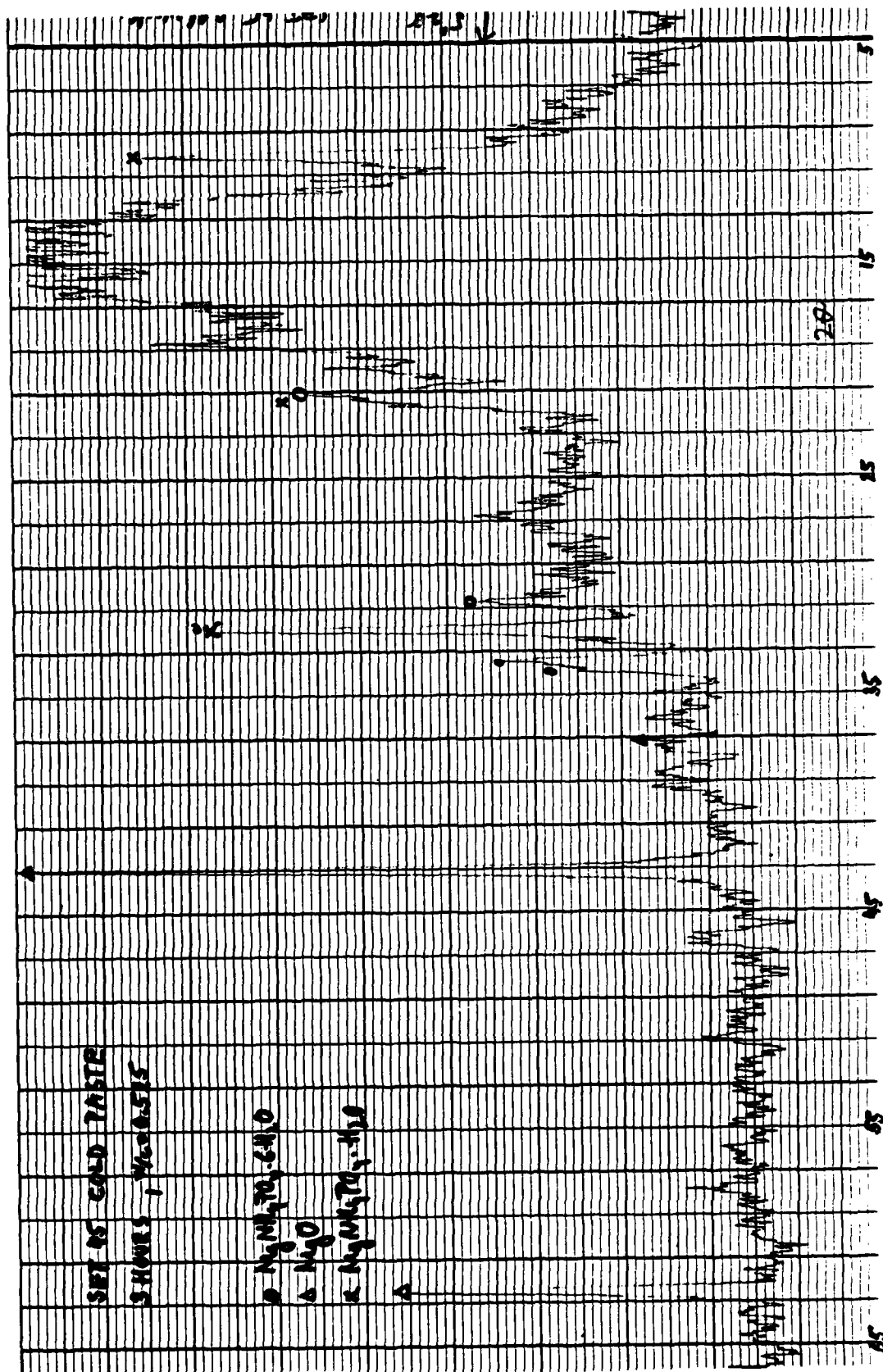


Fig. 40 - X-ray diffraction pattern of SET-45 cold weather paste of high water content at 3 hours.

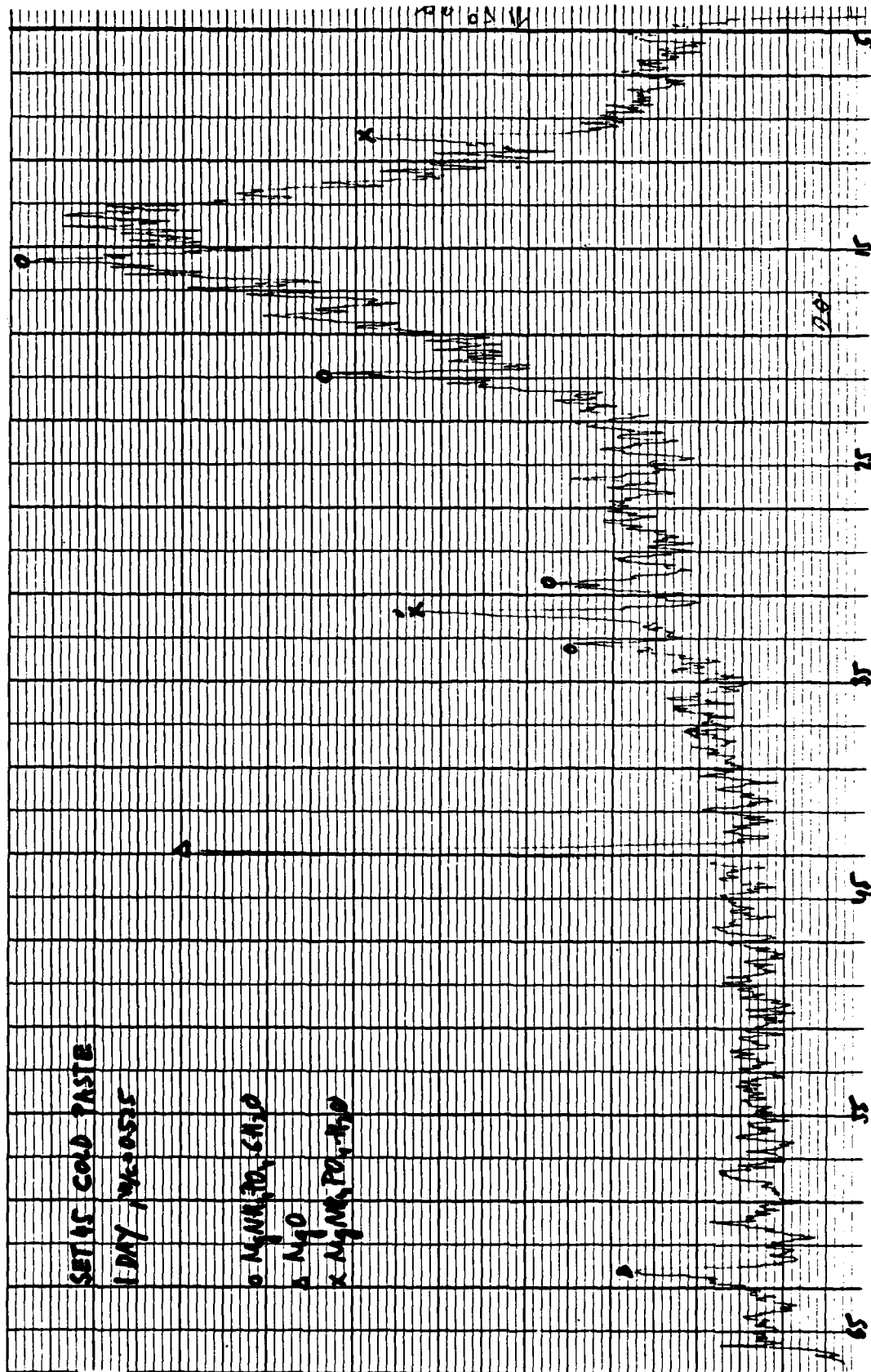


Fig. 41 - X-ray diffraction pattern of SET-45 cold weather paste of high water content at 1 day.

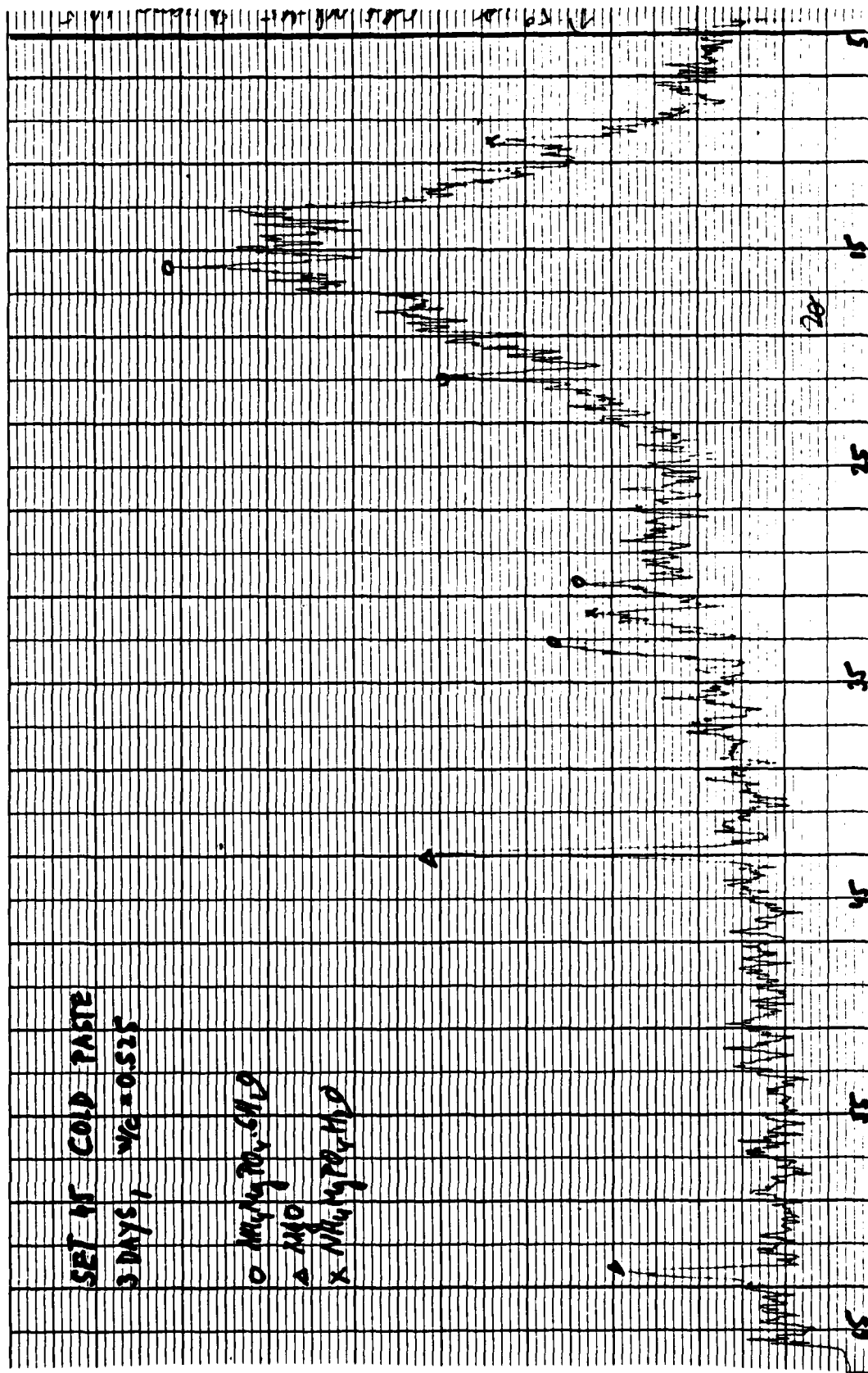


Fig. 42 - X-ray diffraction pattern of SET-45 cold weather paste of high water content at 3 days.

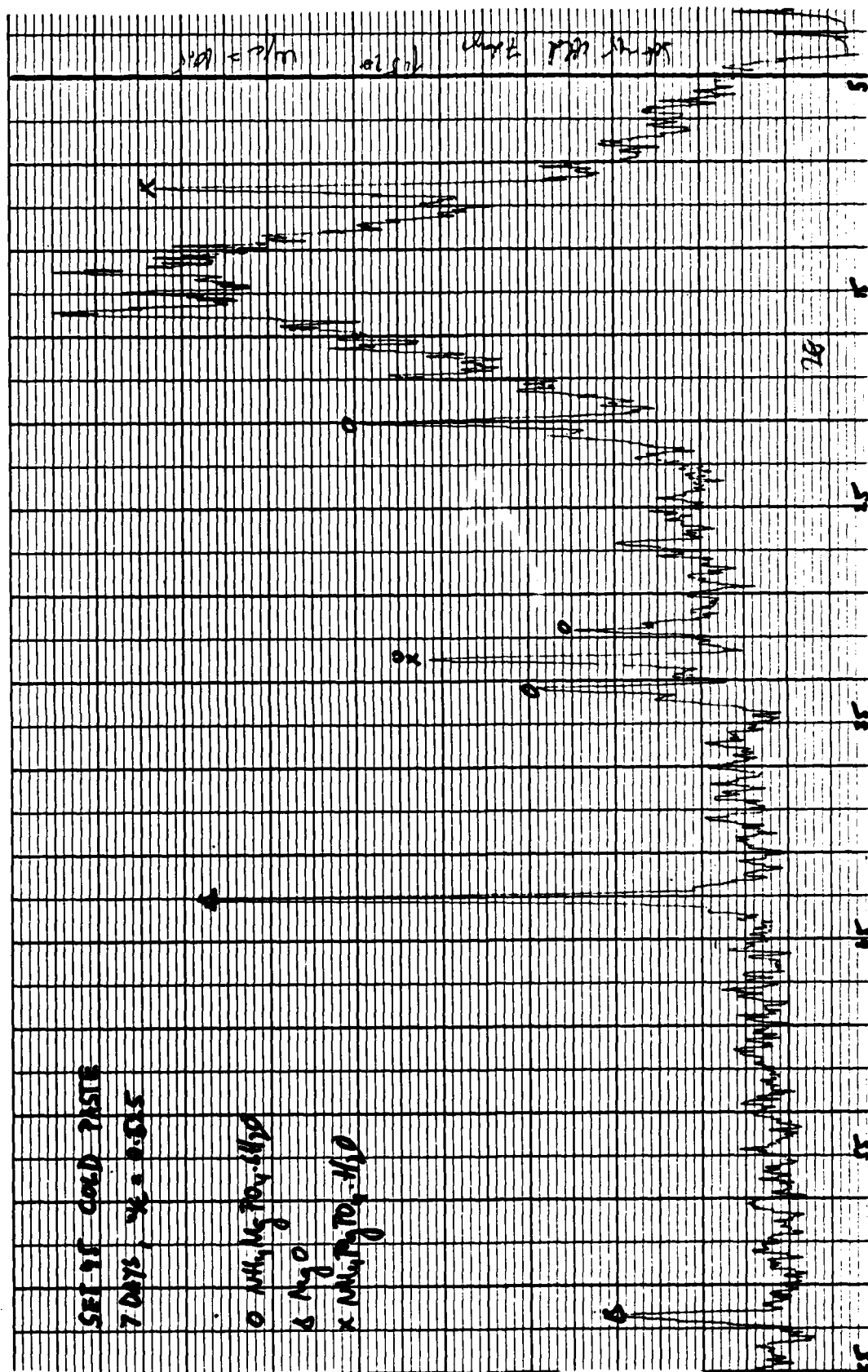


Fig. 43 - X-ray diffraction pattern of SET-45 cold weather paste of high water content at 7 days.

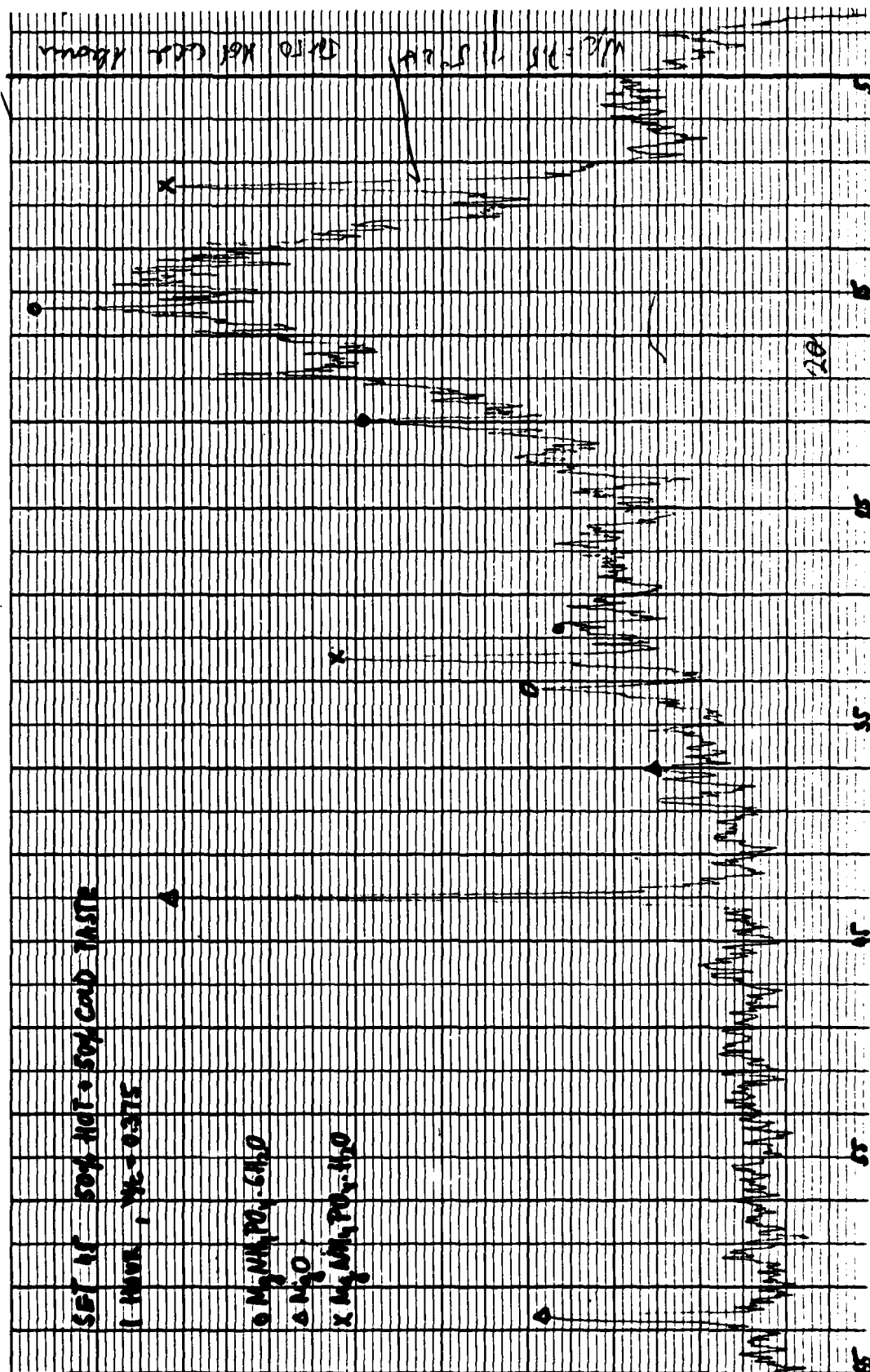


Fig. 44 - X-ray diffraction pattern of SET-45 cold:hot = 1:1 paste of low water content at 1 hour.

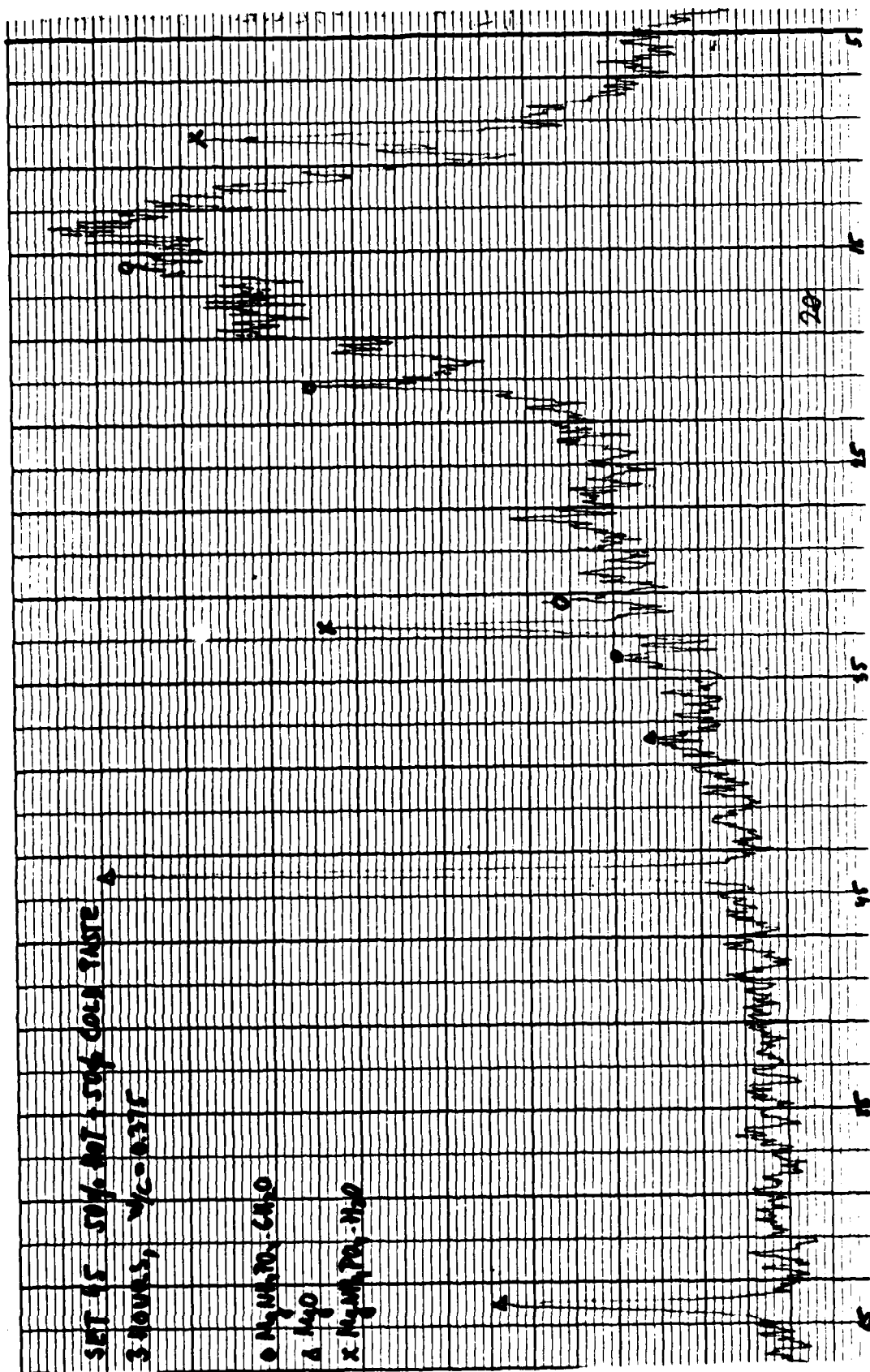


Fig. 45 - X-ray diffraction pattern of SET-45 cold:hot = 1:1 paste of low water content at 3 hours.

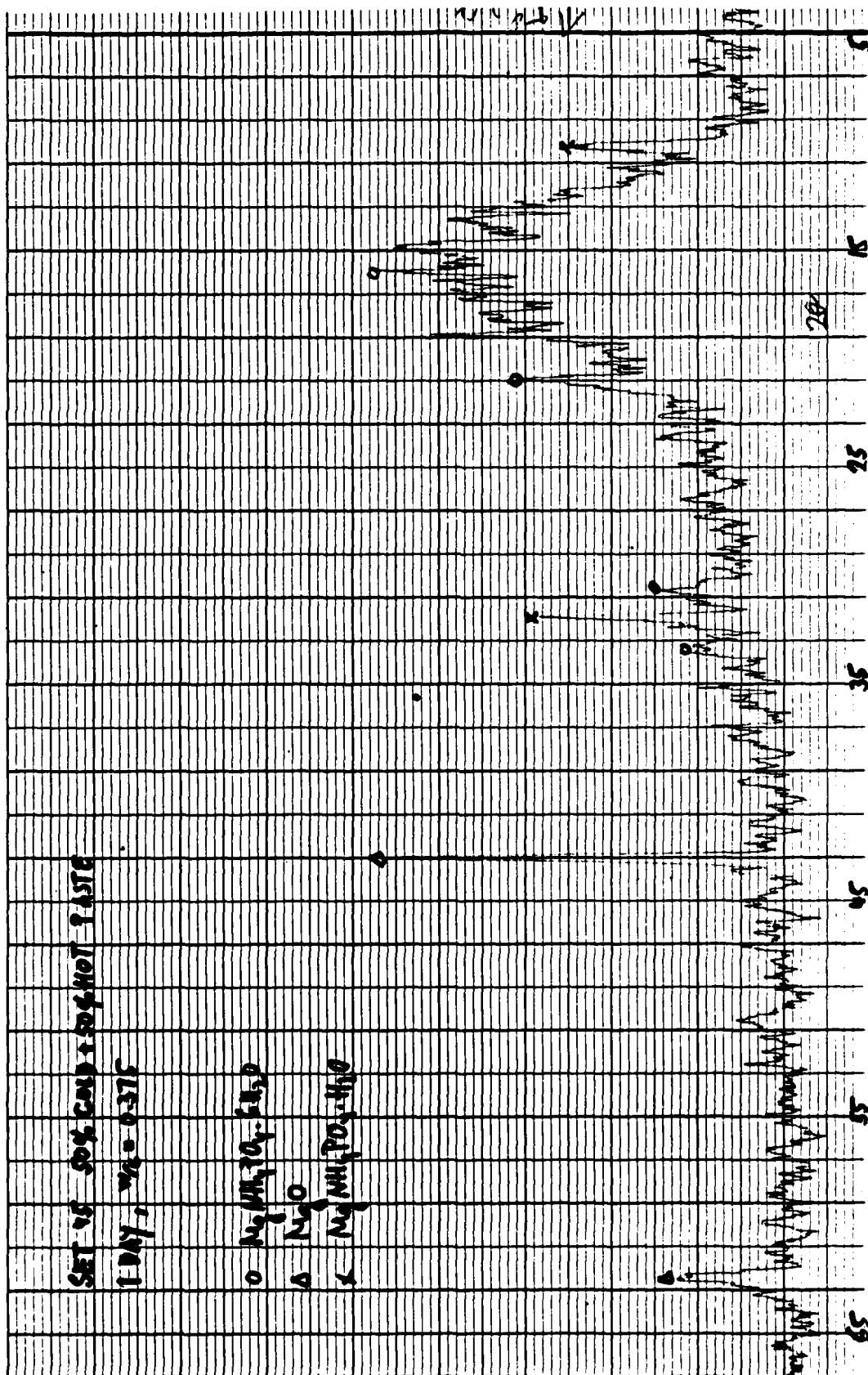


Fig. 46 - X-ray diffraction pattern of SET-45 cold:hot = 1:1 paste of low water content at 1 day.

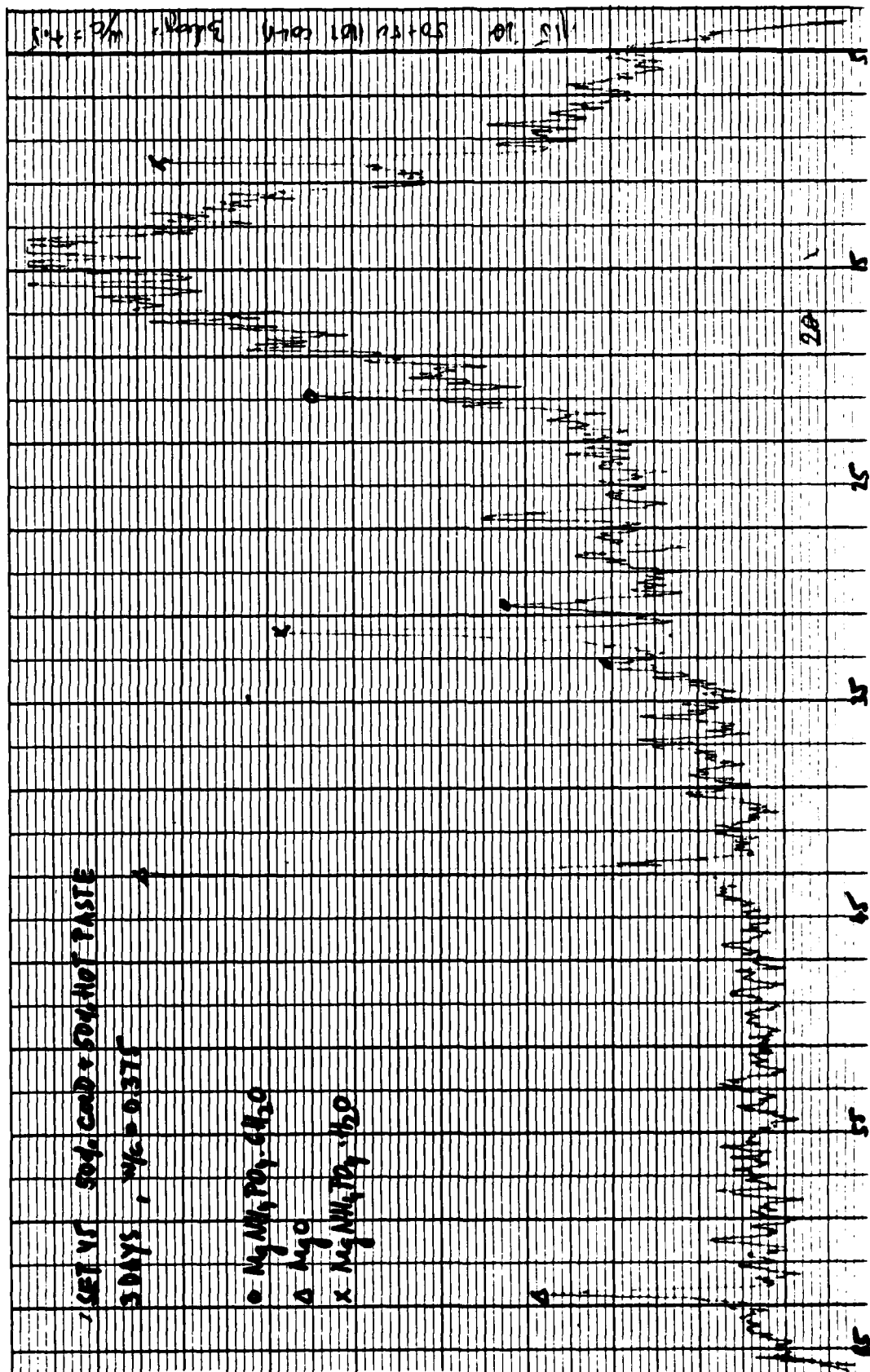


Fig. 47 - X-ray diffraction pattern of SET-45 cold:hot = 1:1 paste of low water content at 3 days.

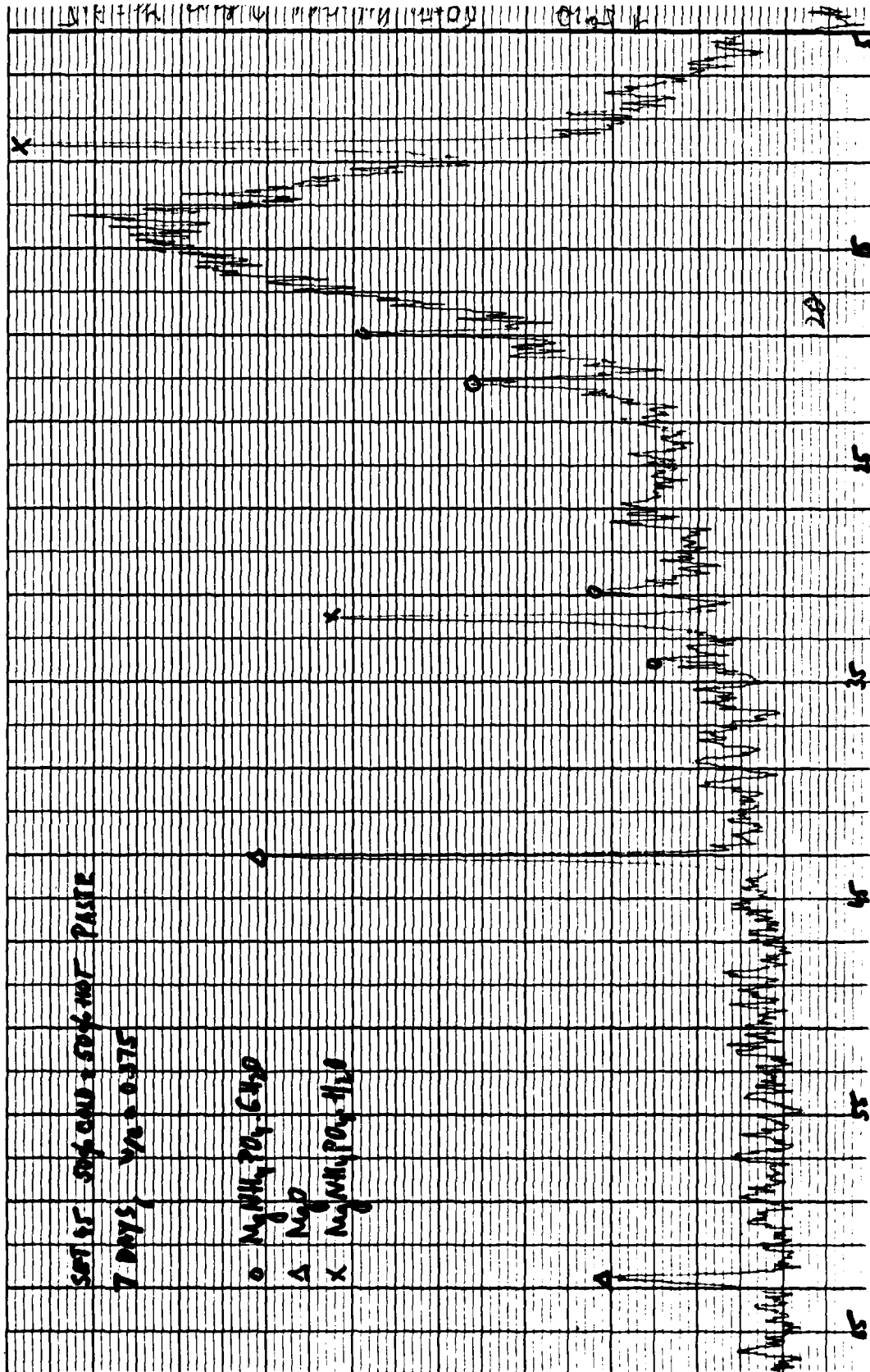


Fig. 48 - X-ray diffraction pattern of SET-45 cold:hot = 1:1 paste of low water content at 7 days.

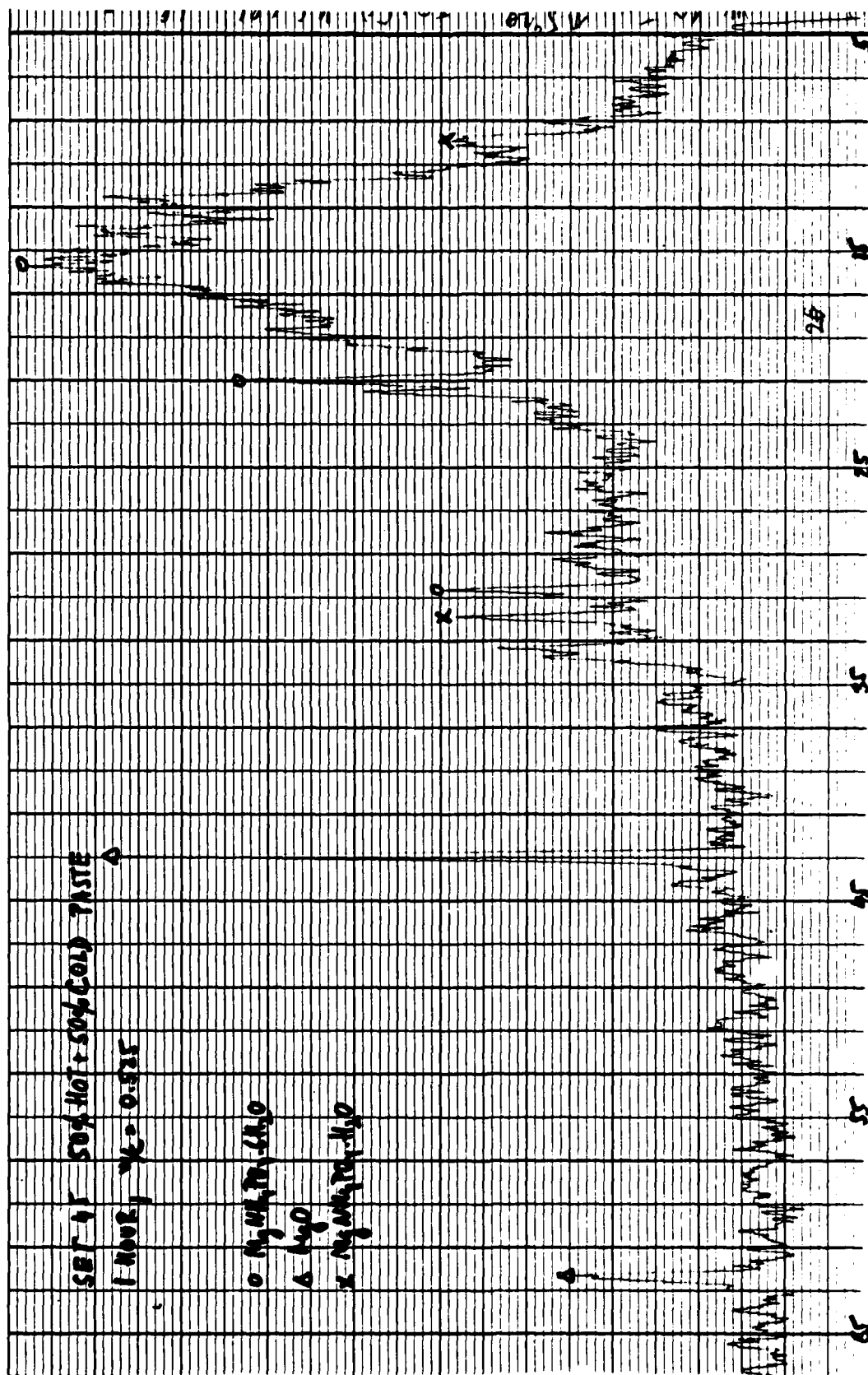


Fig. 49 - X-ray diffraction pattern of SET-45 cold:hot = 1:1 paste of high water content at 1 hour.

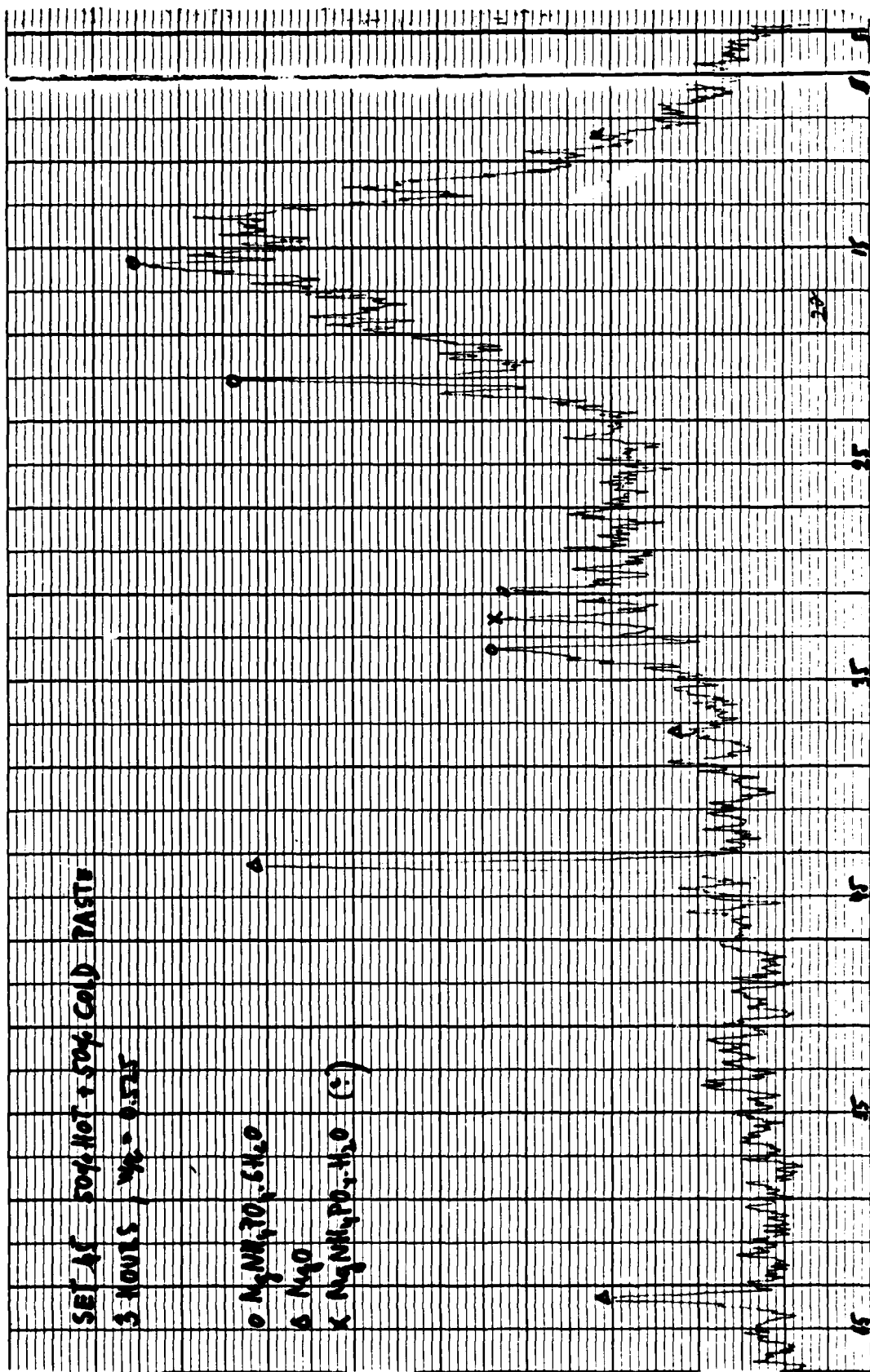


Fig. 50 - X-ray diffraction pattern of SET-45 cold:hot = 1:1 paste of high water content at 3 hours.

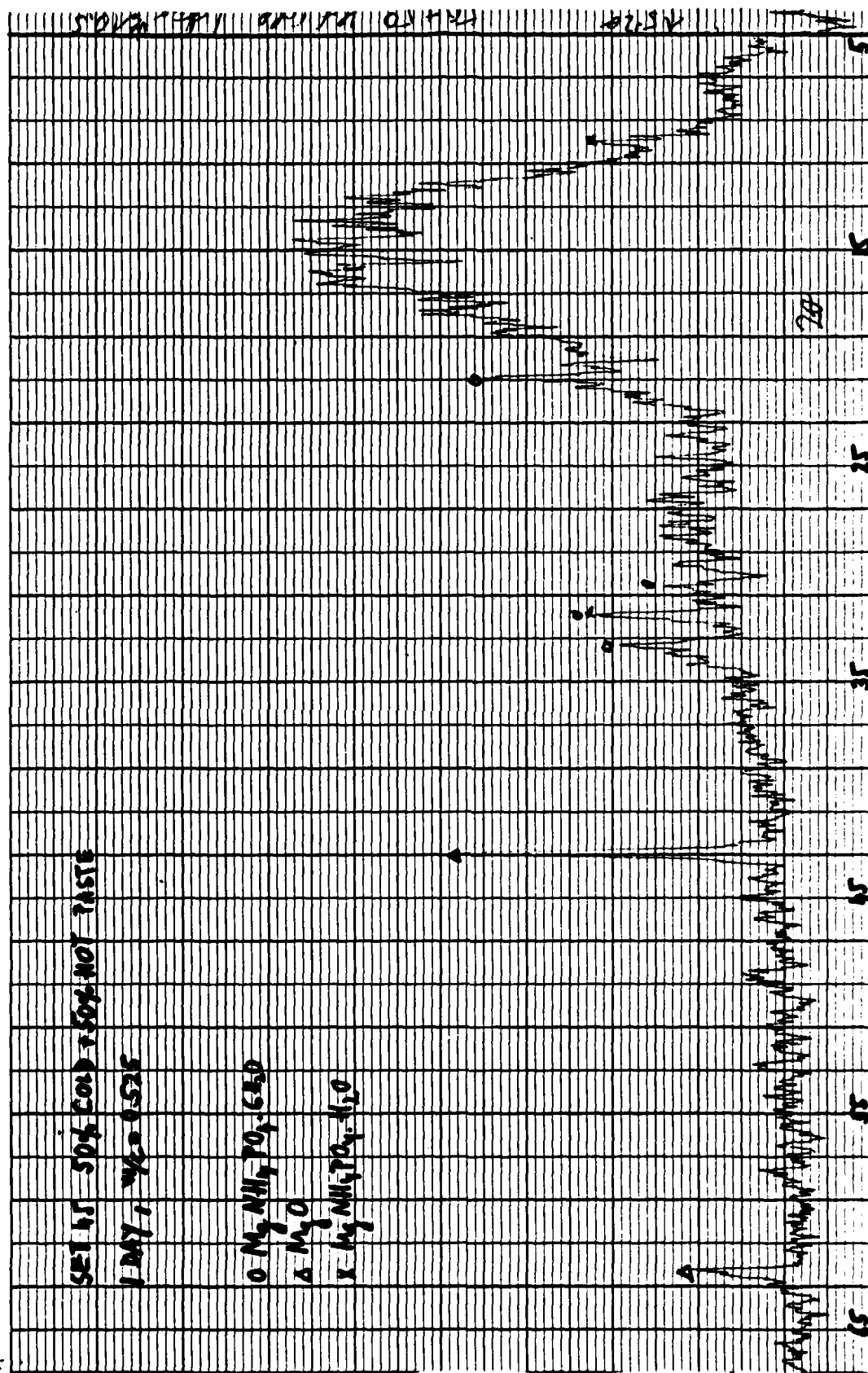


Fig. 51 - X-ray diffraction pattern of SET-45 cold:hot = 1:1 paste of high water content at 1 day.

Fig. 52 ~ X-ray diffraction pattern of SET-45 cold:hot = 1:1 paste of high water content at 3 days.

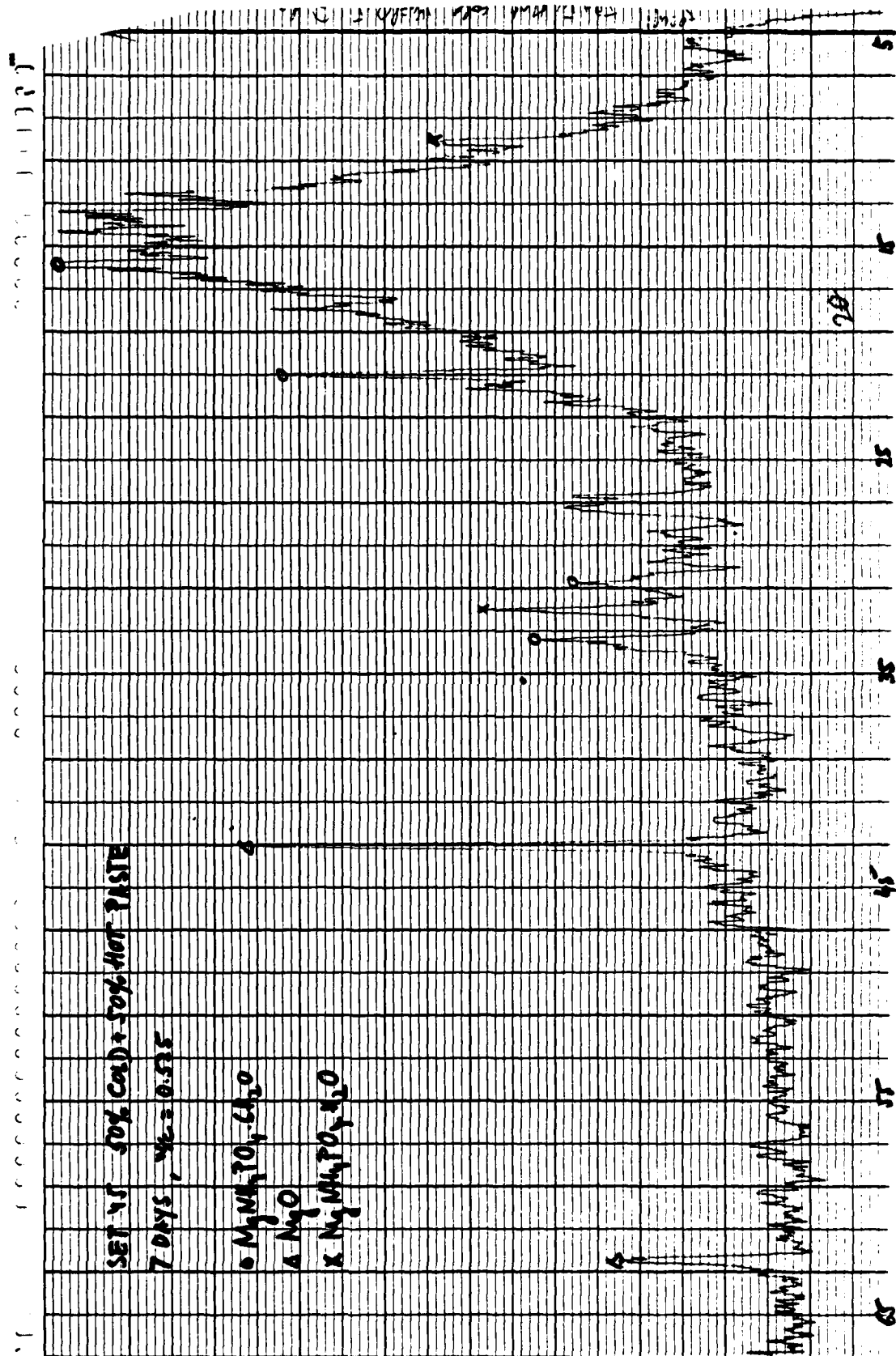


Fig. 53 - X-ray diffraction pattern of SET-45 cold:hot = 1:1 paste of high water content at 7 days.

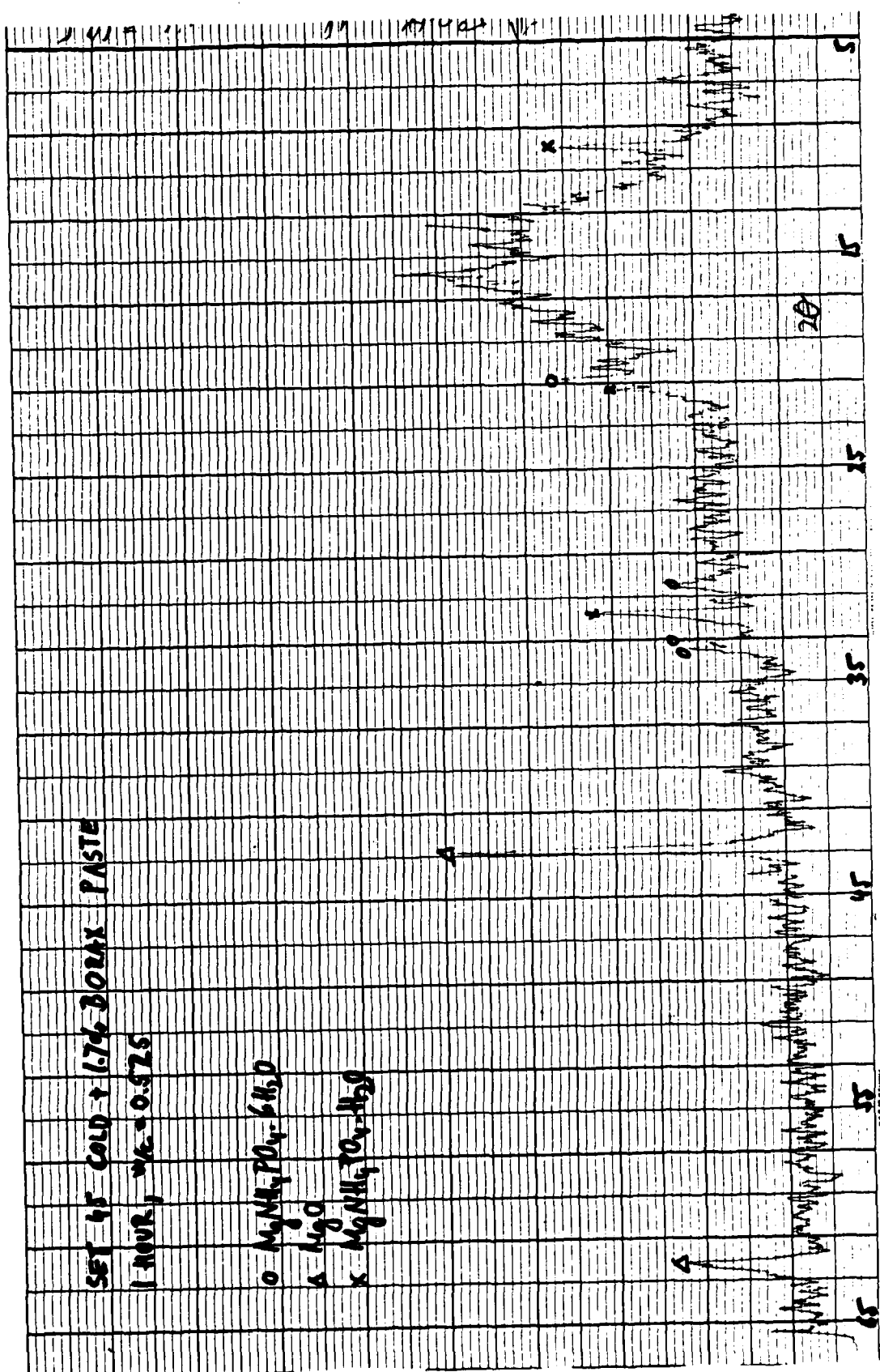


Fig. 54 - X-ray diffraction pattern of SET-45 cold weather paste of high water content with 1.7% borax at 1 hour.

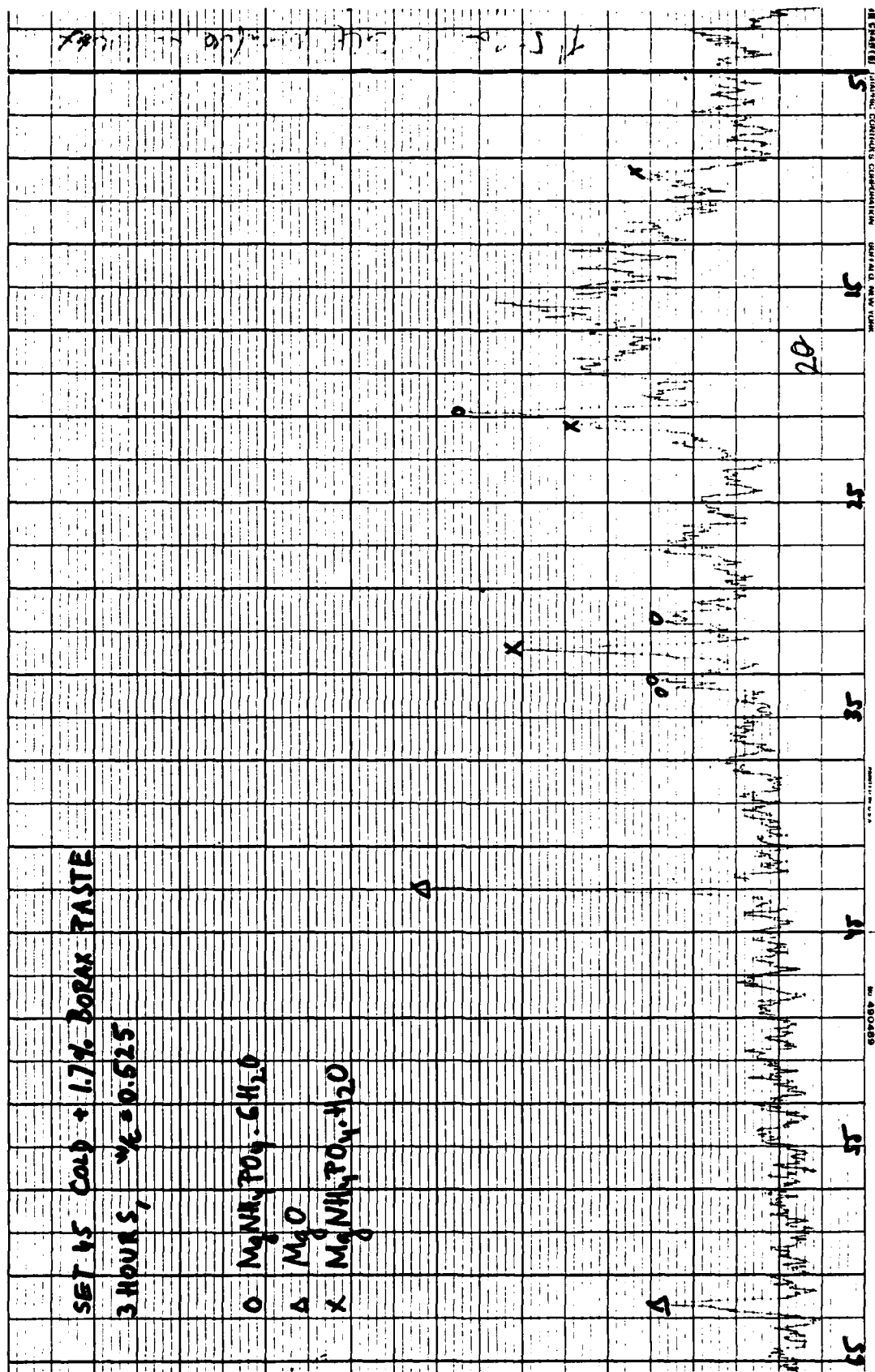


Fig. 55 - X-ray diffraction pattern of SET-45 cold weather paste with 1.7% borax at 3 hours.

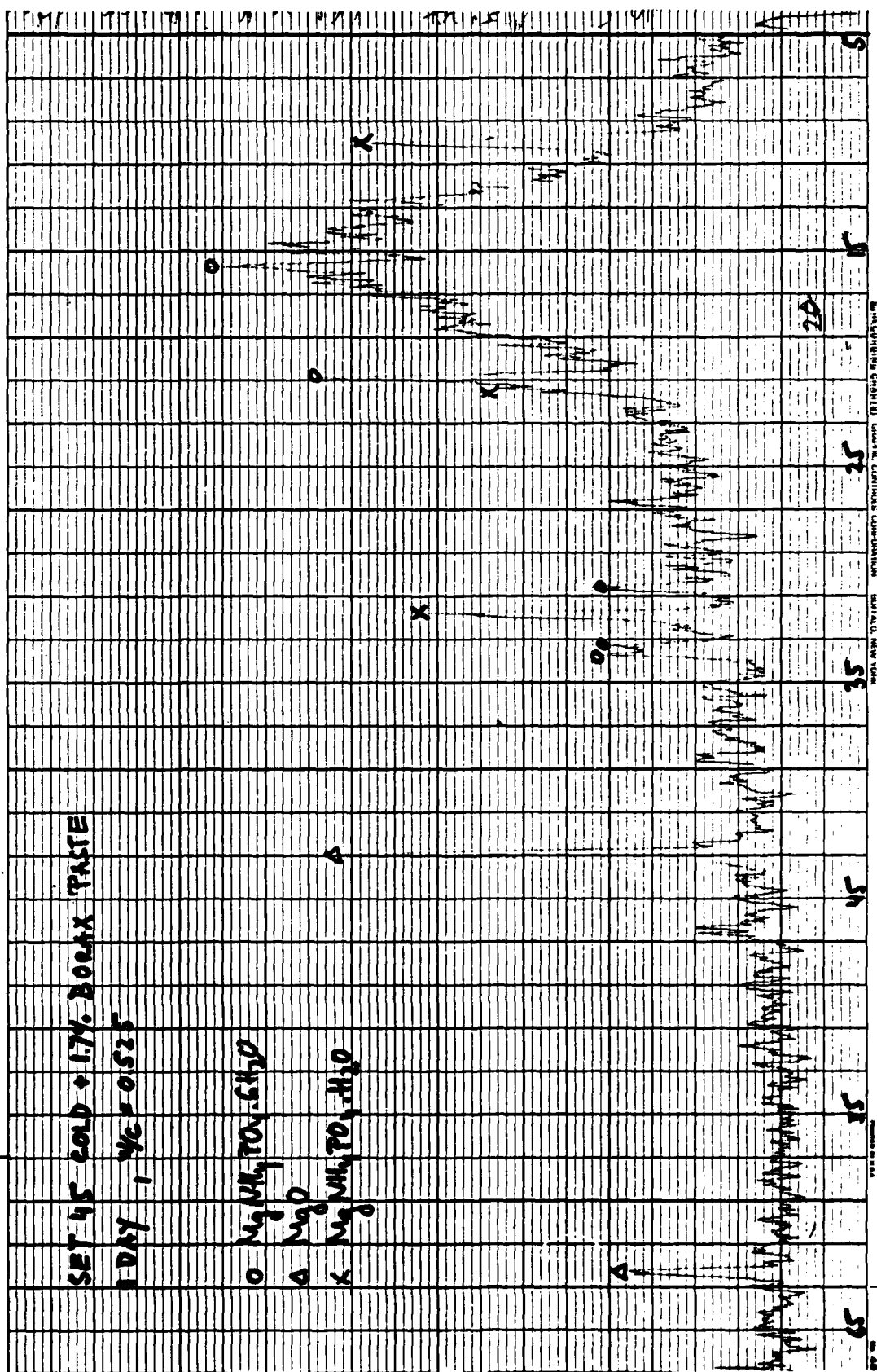


Fig. 56 - X-ray diffraction pattern of SET-45 cold weather paste with 1.7% borax at 1 day.

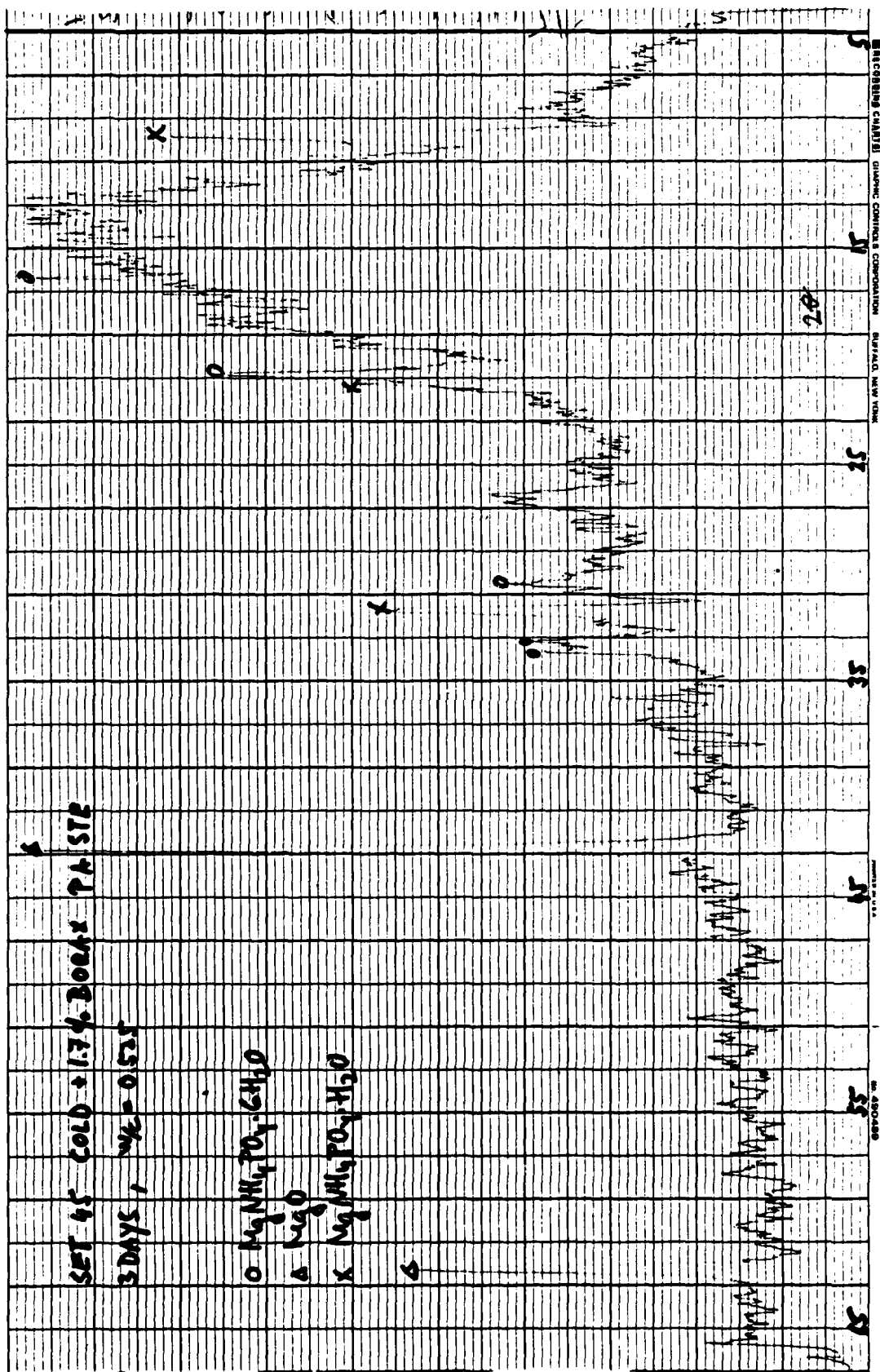


Fig. 57 - X-ray diffraction pattern of SET-45 cold weather paste of high water content with 1.7% borax at 3 days.

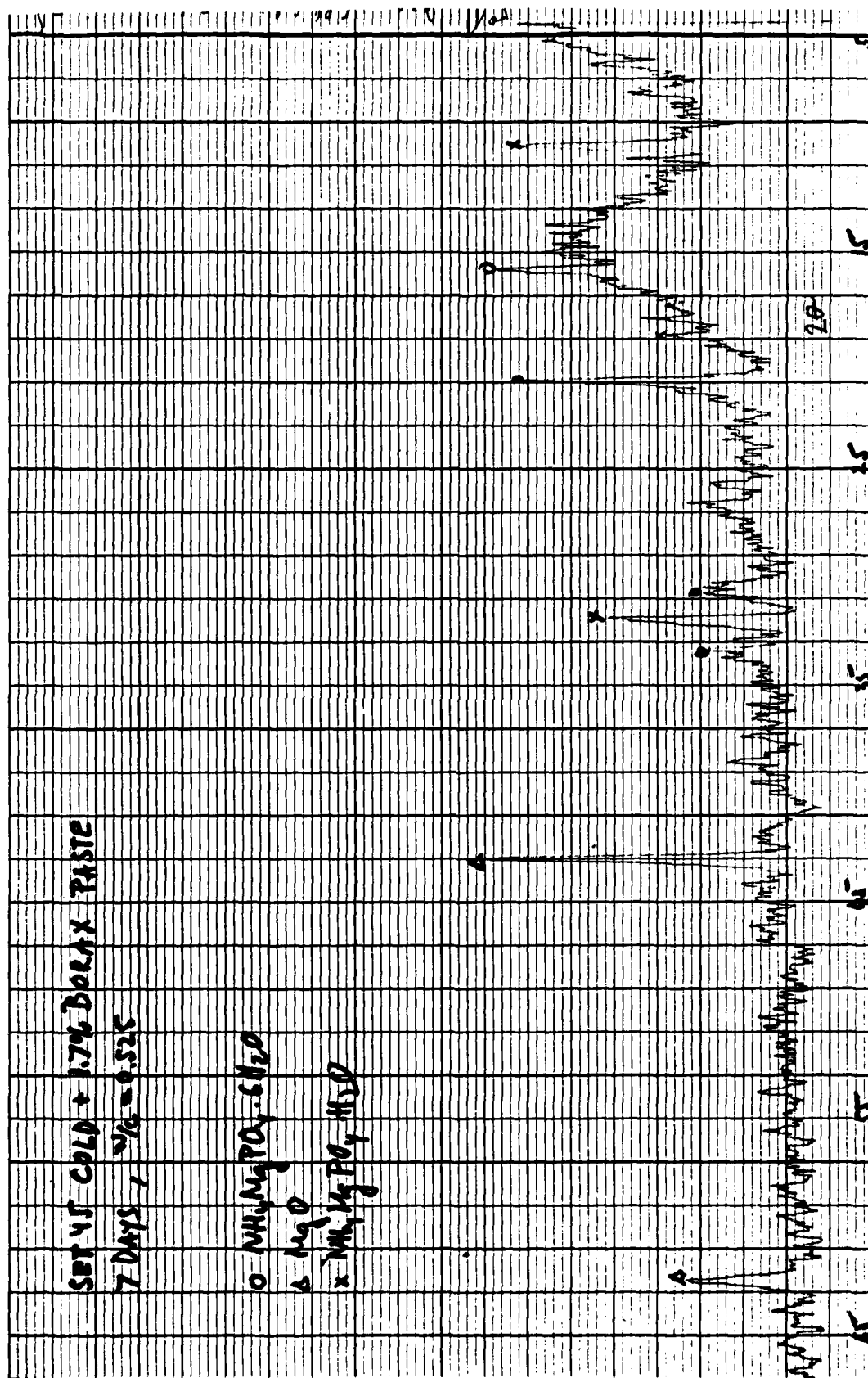


Fig. 58 - X-ray diffraction pattern of SET-45 cold weather paste with 1.7% borax at 7 days.

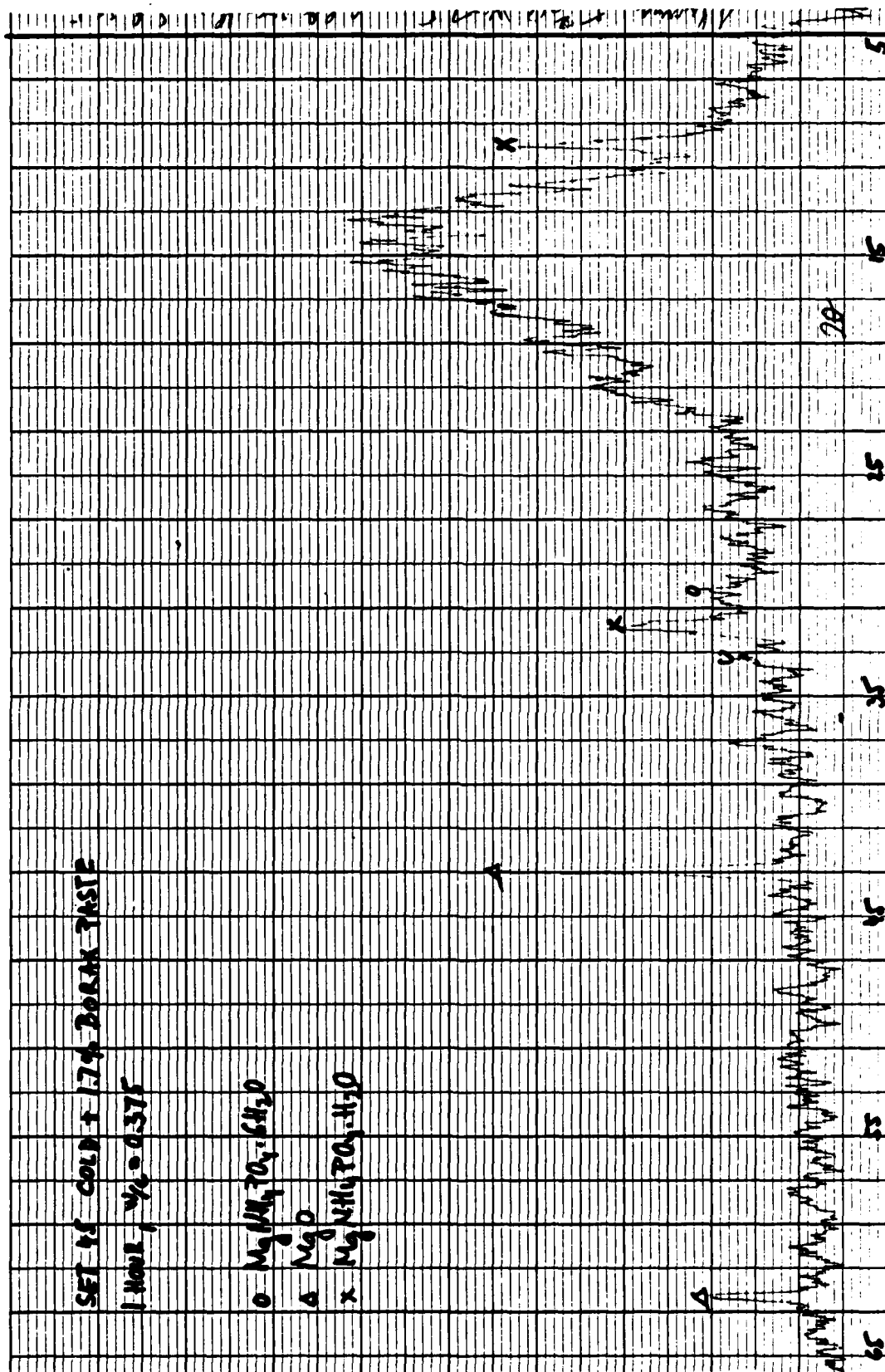


Fig. 59 - X-ray diffraction pattern of SET-45 cold weather paste of low water content with 1.7% borax at 1 hour.

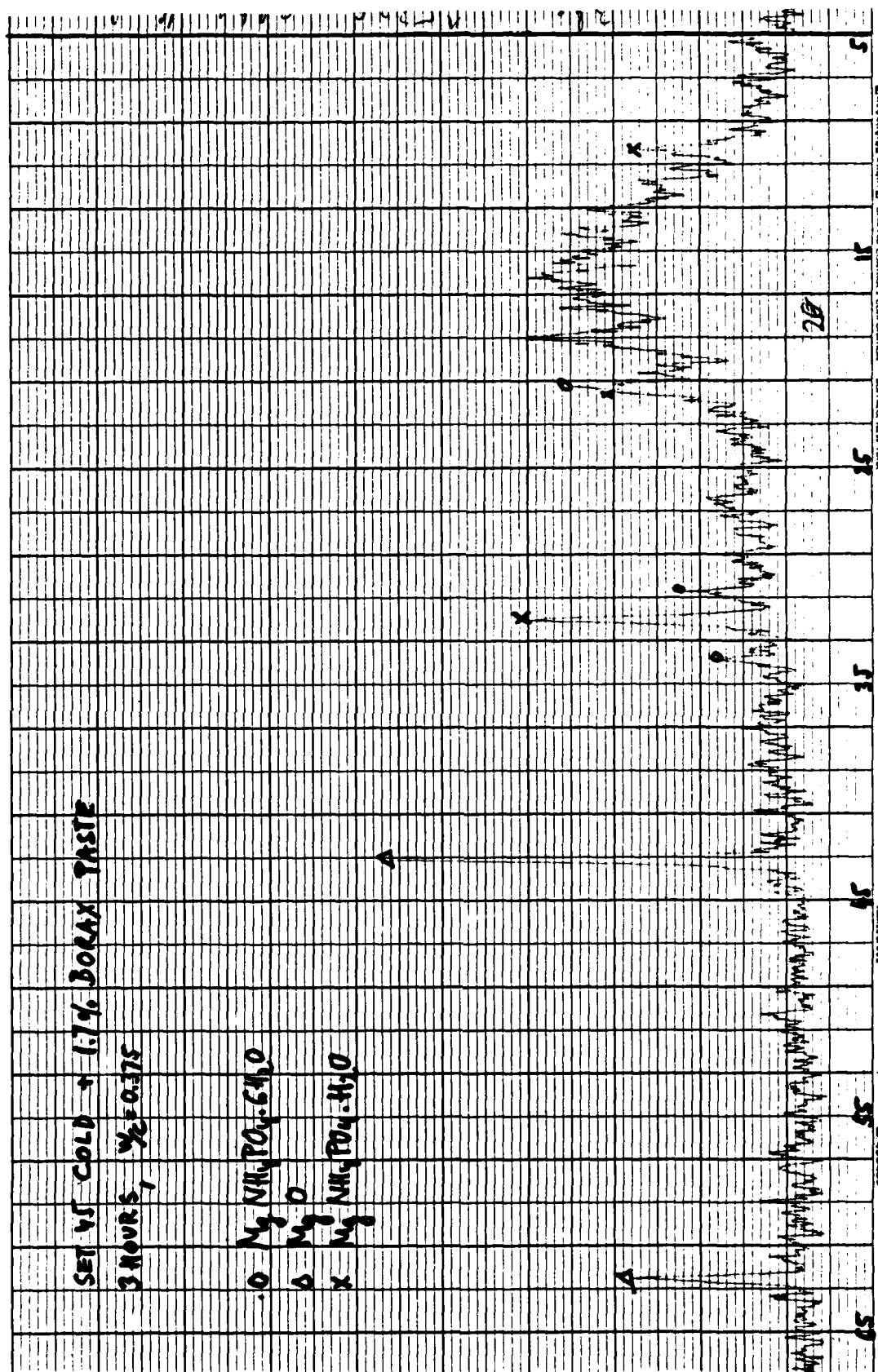


Fig. 60 - X-ray diffraction pattern of SET-45 cold weather paste of low water content with 1.7% borax at 3 hours.

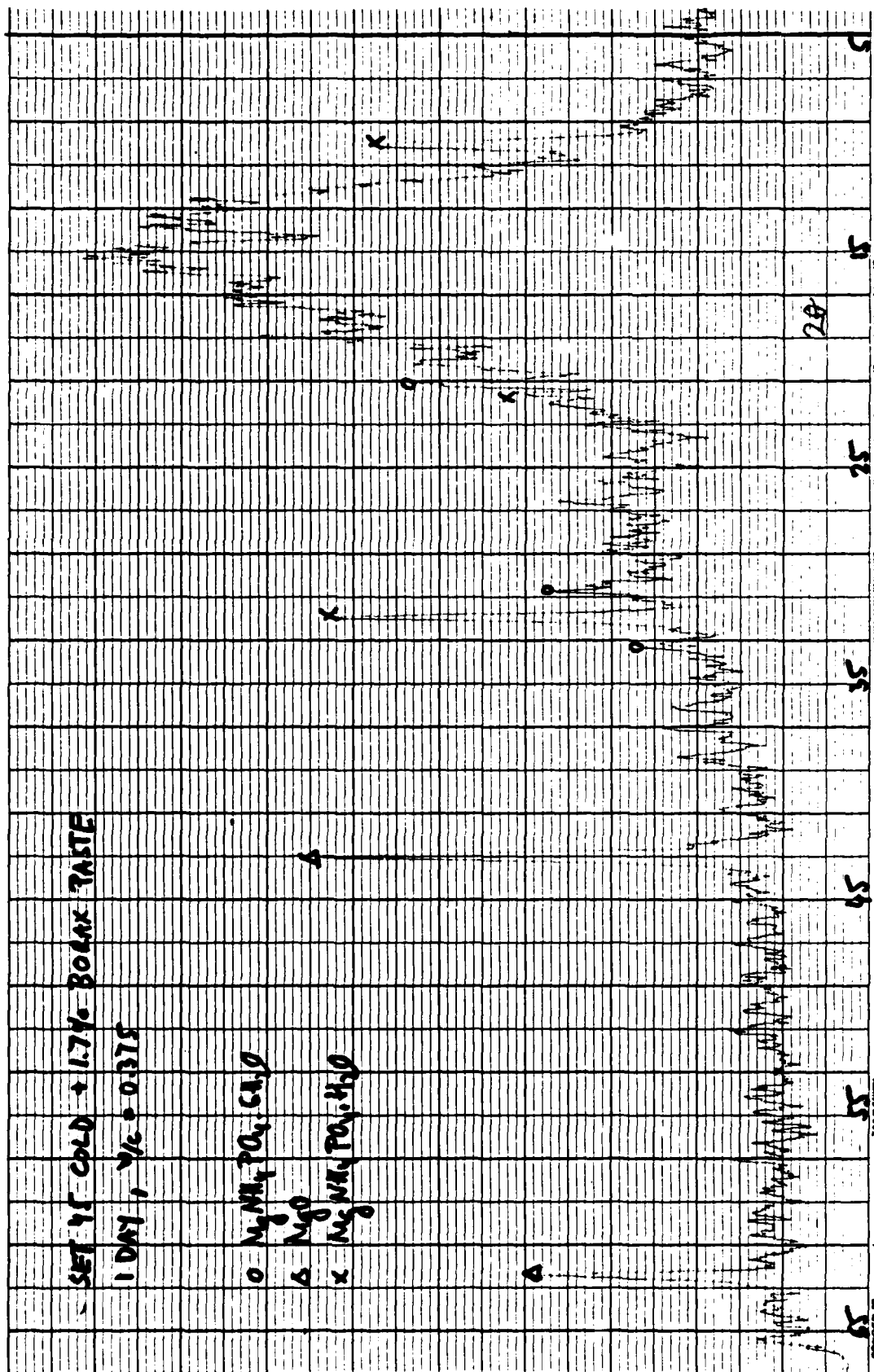


Fig. 61 - X-ray diffraction pattern of SET-45 cold weather paste of low water content with 1.7% borax at 1 day.

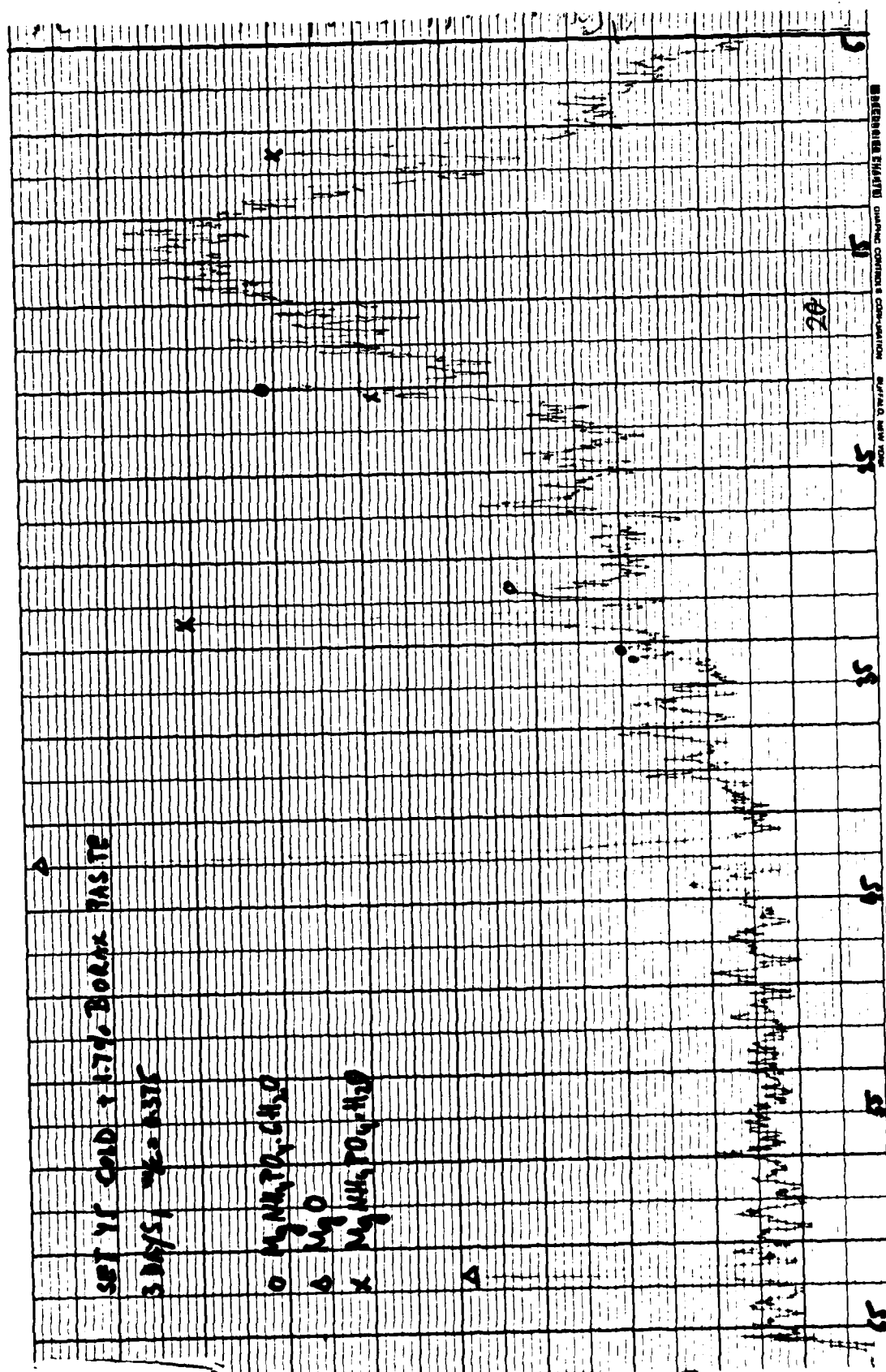


Fig. 62 - X-ray diffracta. pattern of SET-45 cold weather paste of low water content with 1.7% borax at 3 days.

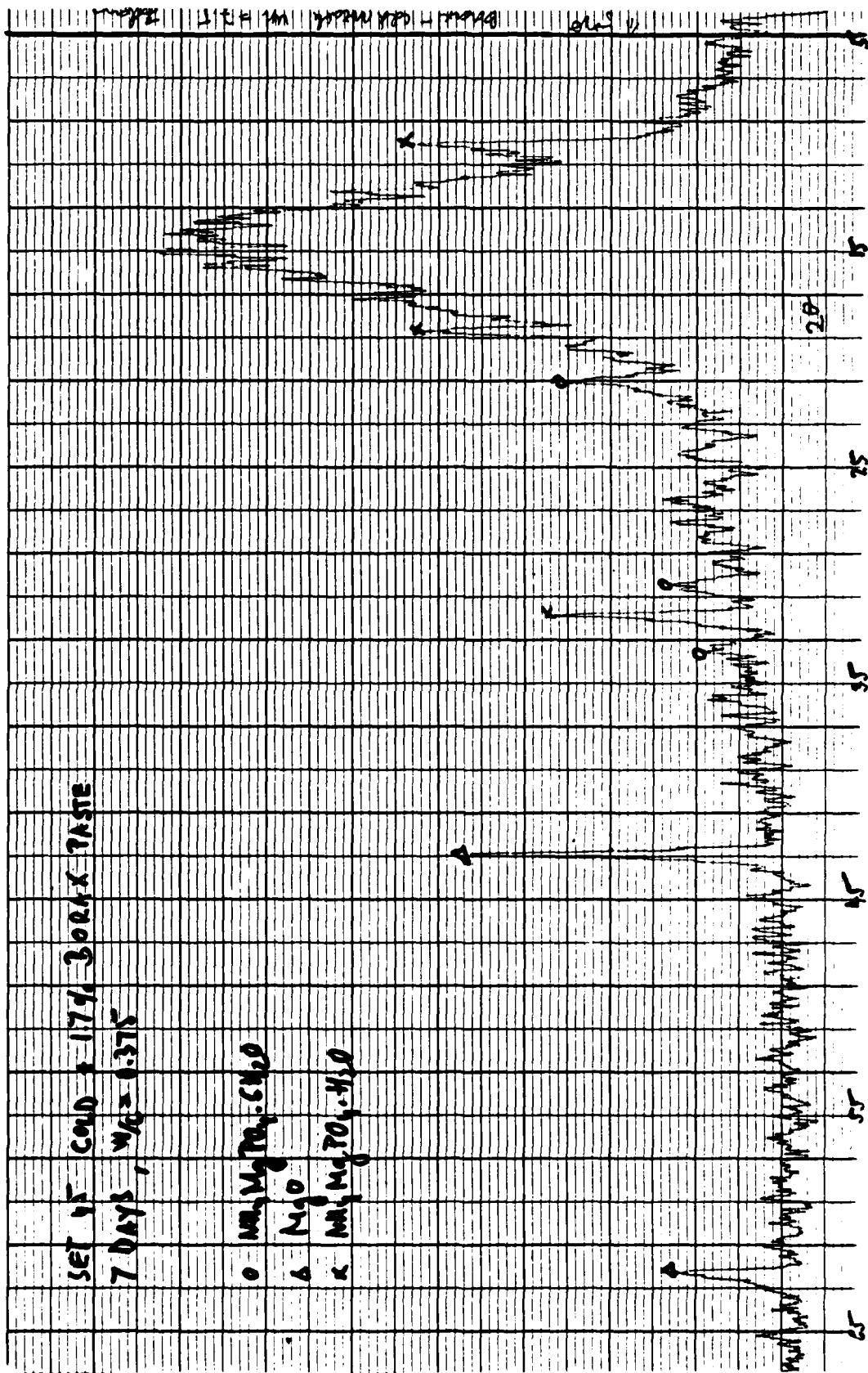


Fig. 63 - X-ray diffraction pattern of SET-45 cold weather paste of low water content with 1.7% borax at 7 days.

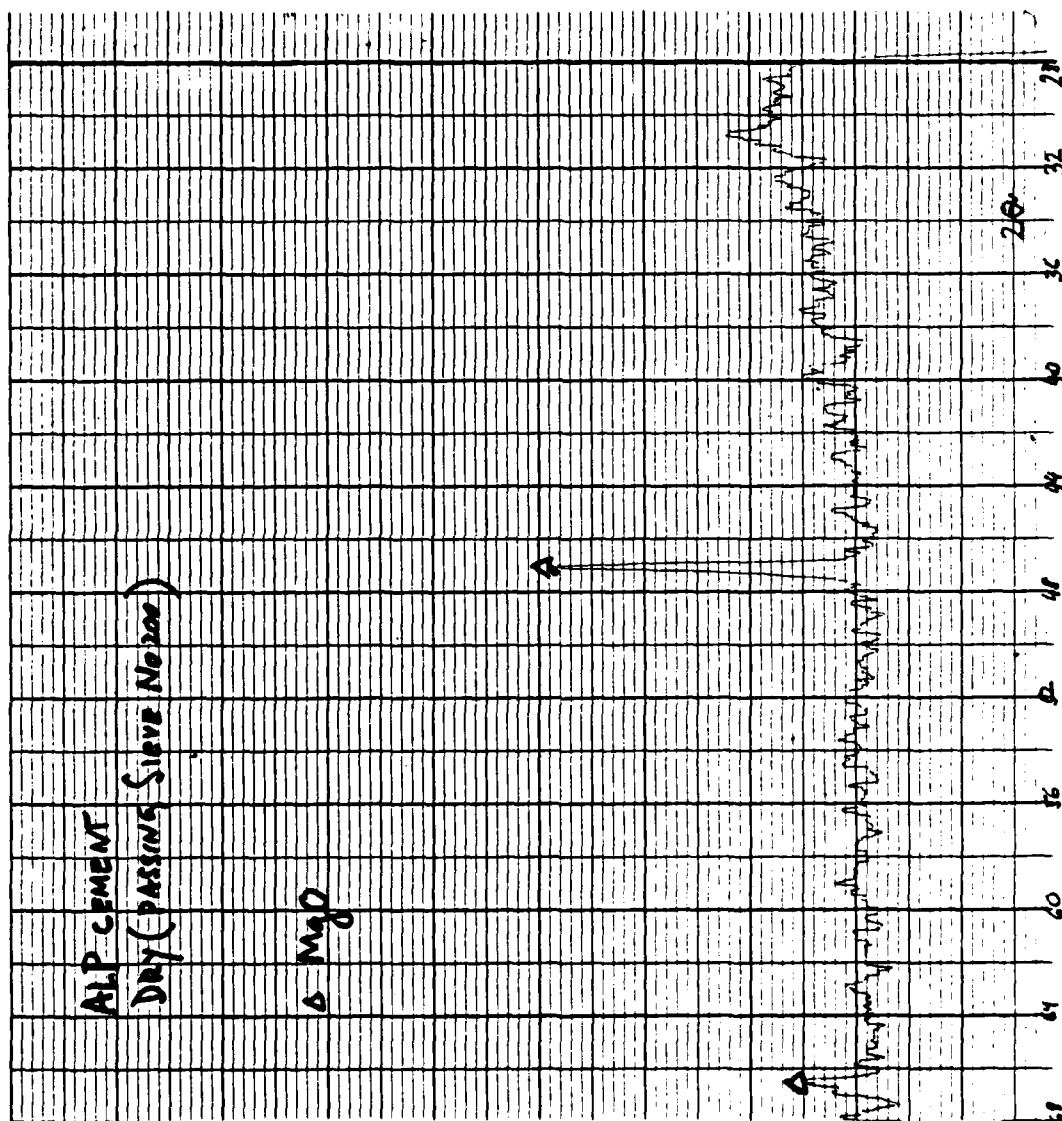


Fig. 64 - X-ray diffraction pattern of ALP cement.

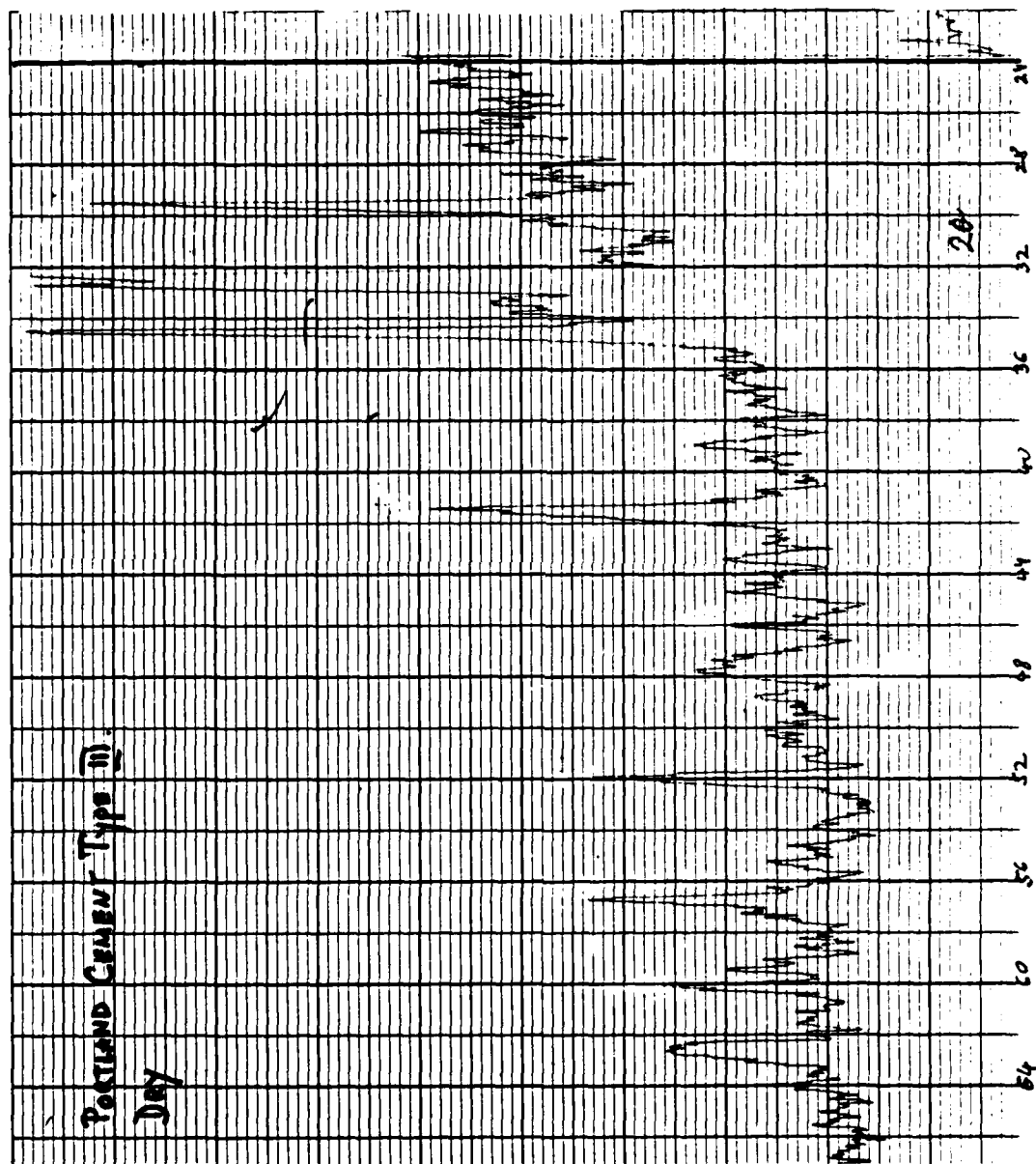


Fig. 65 - X-ray diffraction pattern of portland cement Type III.

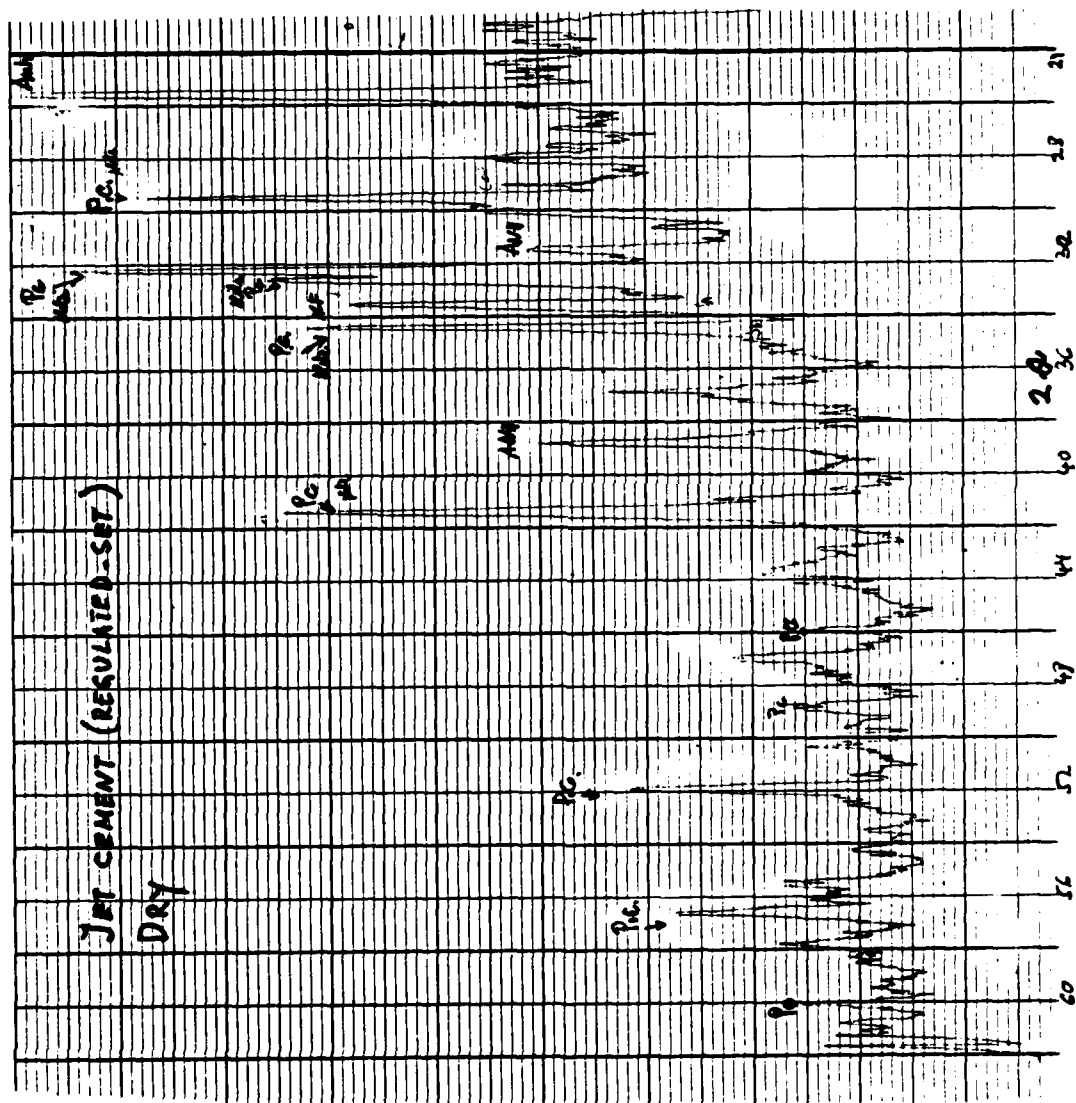


Fig. 66 - X-ray diffraction pattern of Jet cement.

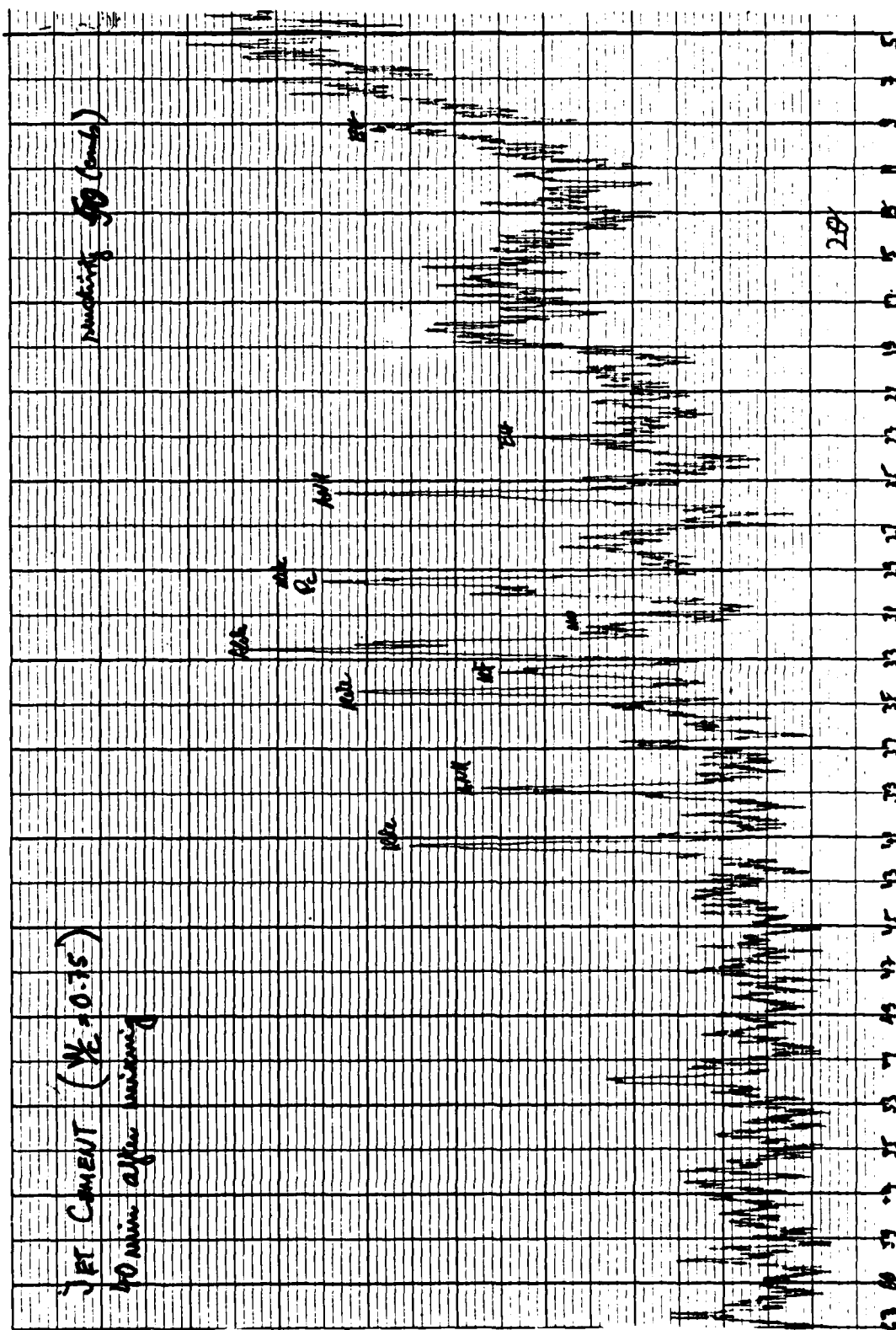


Fig. 67 - X-ray diffraction pattern of Jet cement paste of water-cement ratio 0.75 at 40 minutes.

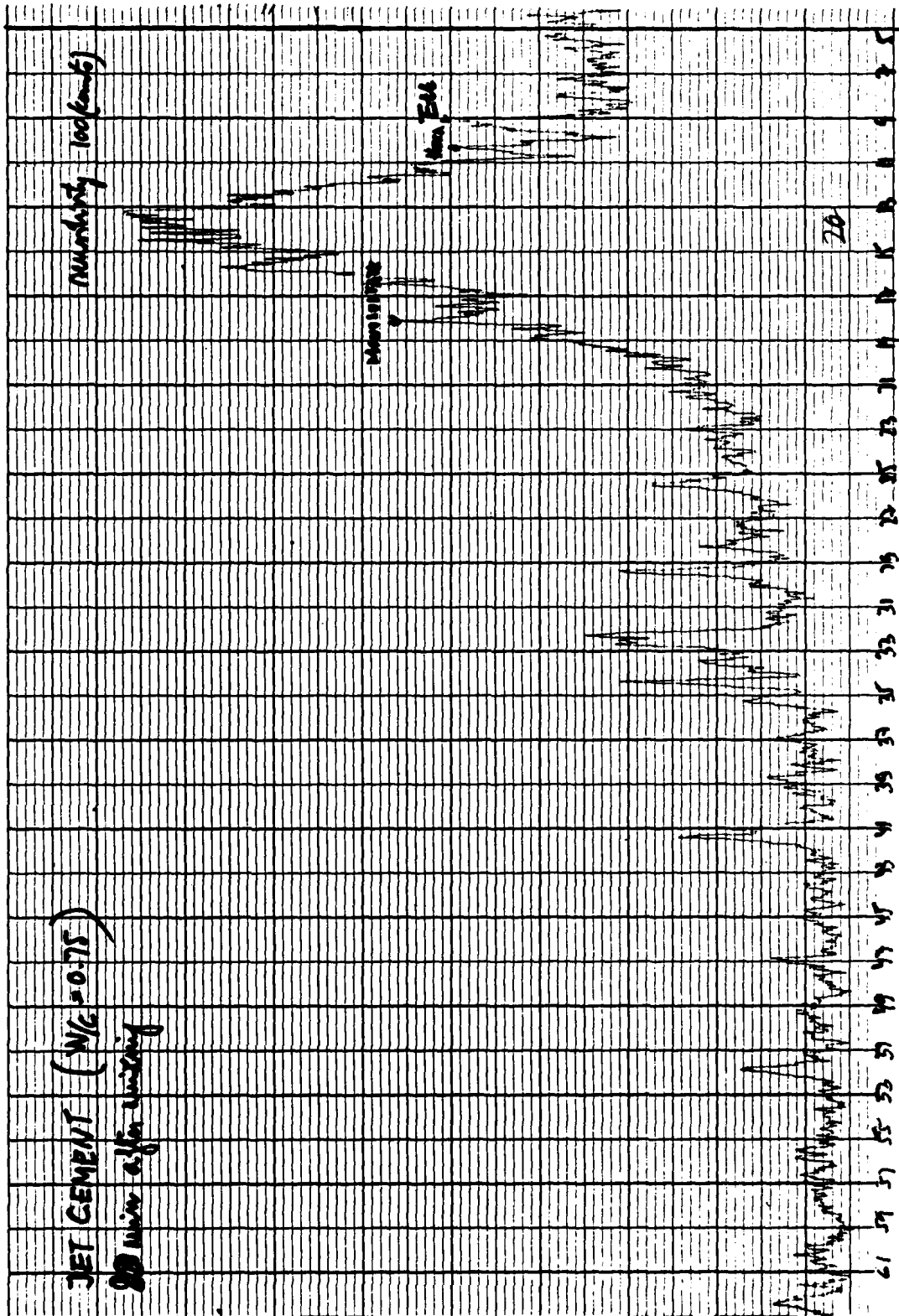


Fig. 68 - X-ray diffraction pattern of Jet cement paste of water-cement ratio 0.75 at 80 minutes.

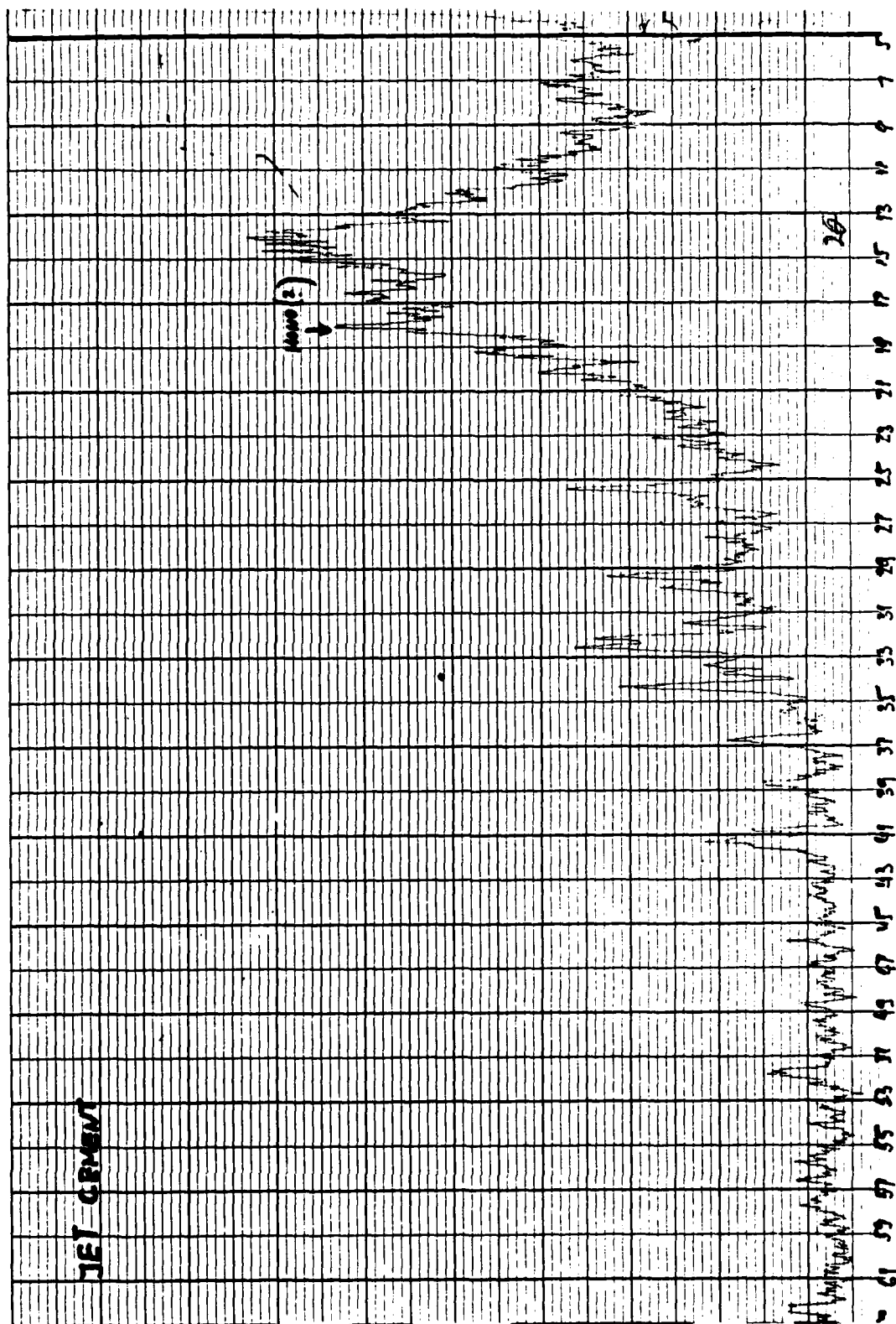


Fig. 69 - X-ray diffraction pattern of Jet cement.

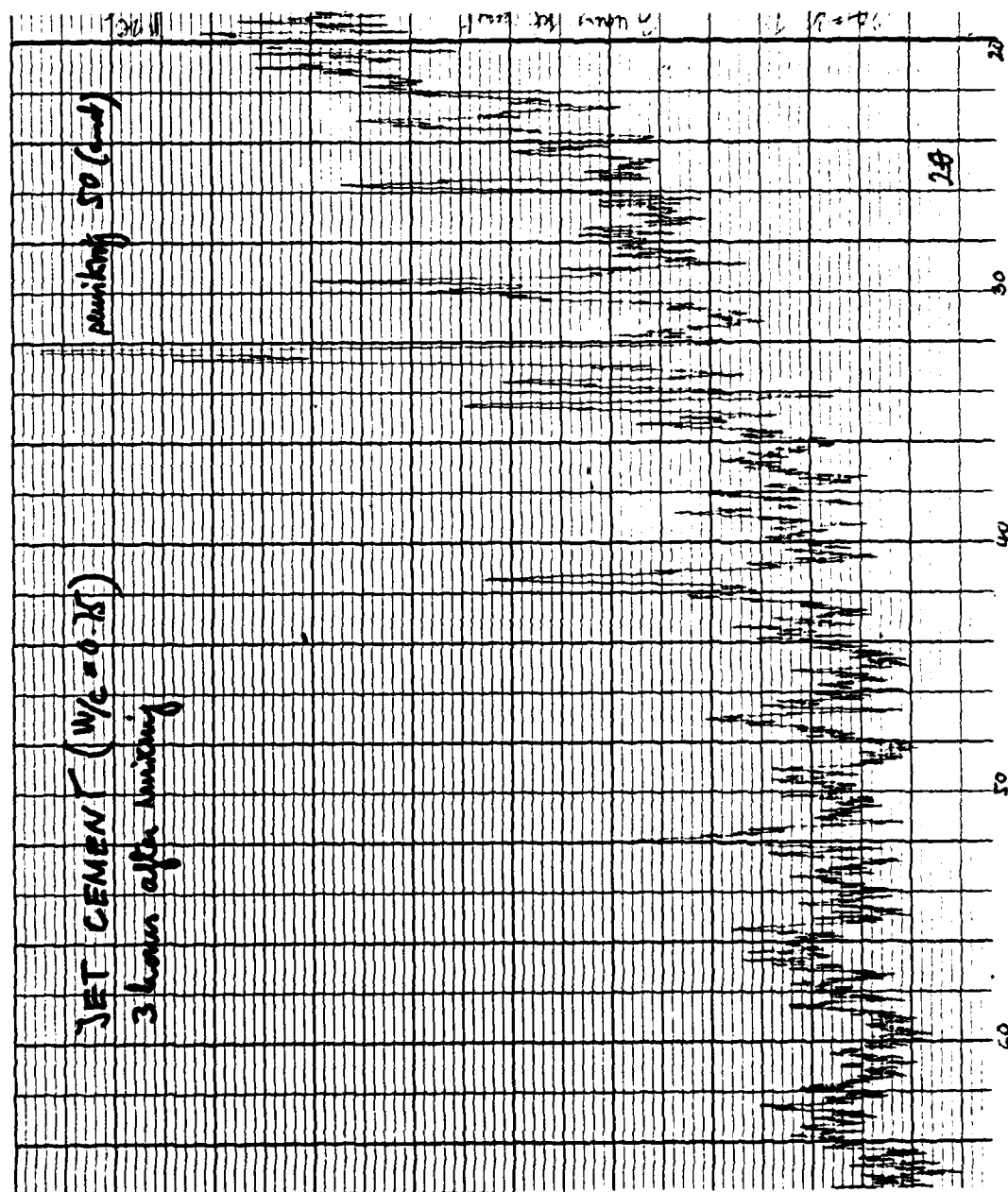


Fig. 70 - X-ray diffraction pattern of Jet cement paste of water-cement ratio 0.75 at 3 hours.

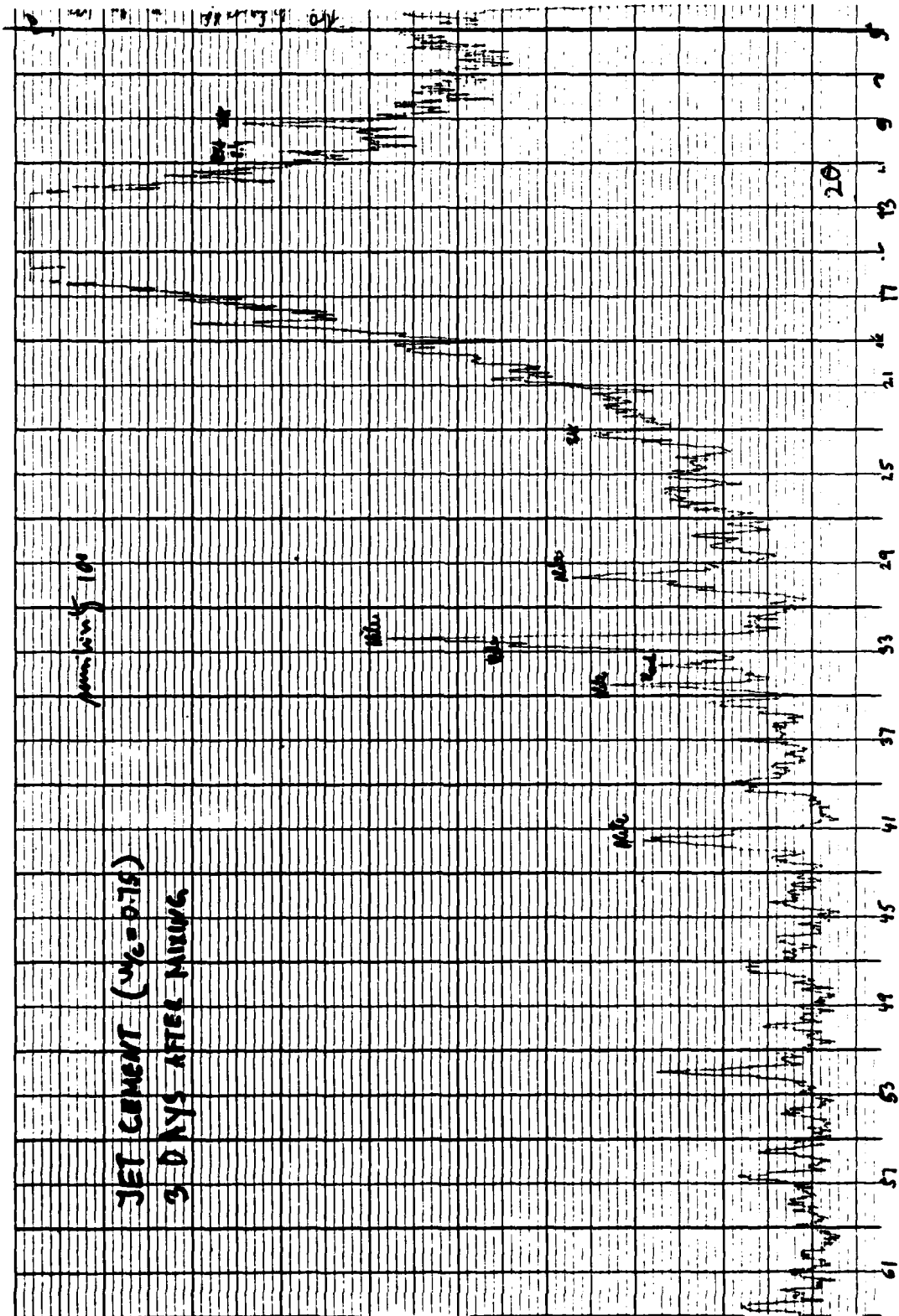


Fig. 71 - X-ray diffraction pattern of Jet cement paste of water-cement ratio 0.75 at 3 hours.

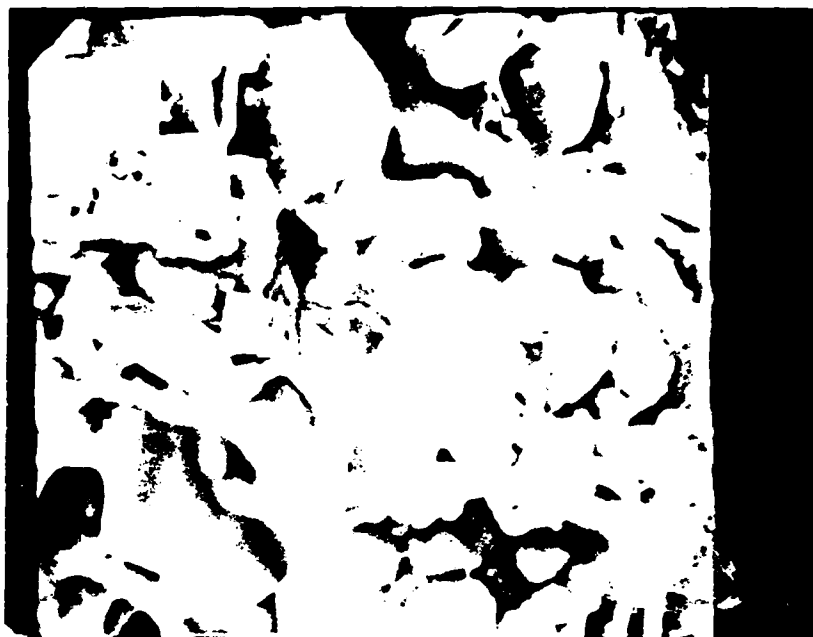


Fig. 72 - SEM picture of SET-45 hot weather paste of high water content at 3 days. Magnification 2000.



Fig. 73 - SEM picture of SET-45 hot weather paste of high water content at 3 days. Magnification 5000.



Fig. 74 - SEM picture of SET-45 cold weather paste of high water content at 3 days. Magnification 2000.



Fig. 75 - SEM picture of SET-45 cold weather paste of high water content at 3 days. Magnification 5000.

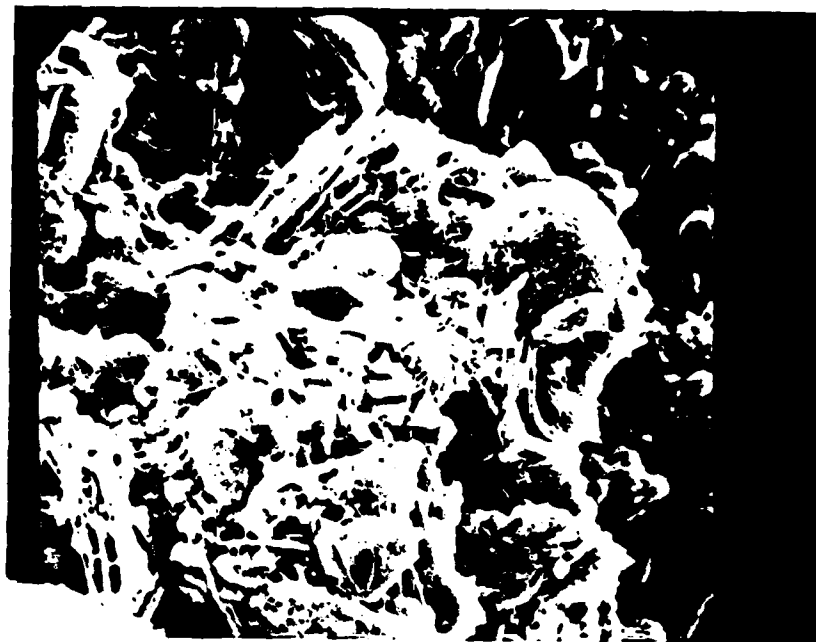


Fig. 76 - SEM picture of SET-45 cold weather paste of high water content with 1.7% borax at 3 days. Magnification 2000.

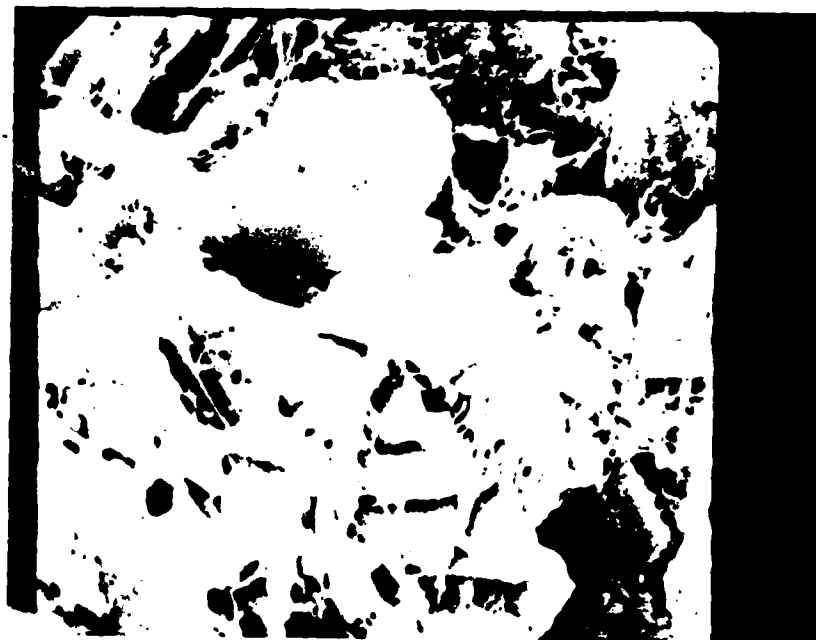


Fig. 77 - SEM picture of SET-45 cold weather paste of high water content with 1.7% borax at 3 days. Magnification 5000.



Fig. 78 - SEM picture of SET-45 hot:cold = 1:1 paste of high water content at 3 days. Magnification 2000.



Fig. 79 - SEM picture of SET-45 hot:cold = 1:1 paste of high water content at 3 days. Magnification 5000.

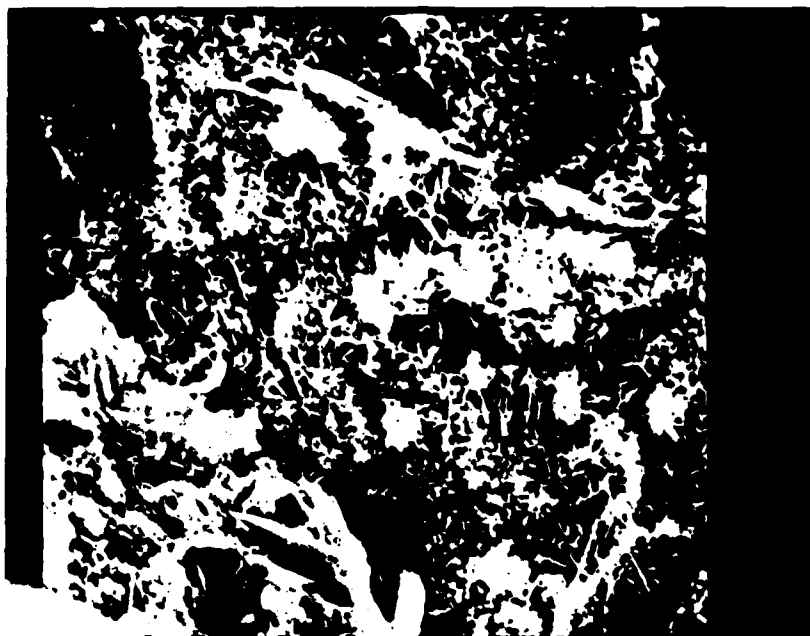


Fig. 80 - SEM picture of portland cement Type III paste of water-cement ratio 0.35 at 1 day. Magnification 2000.

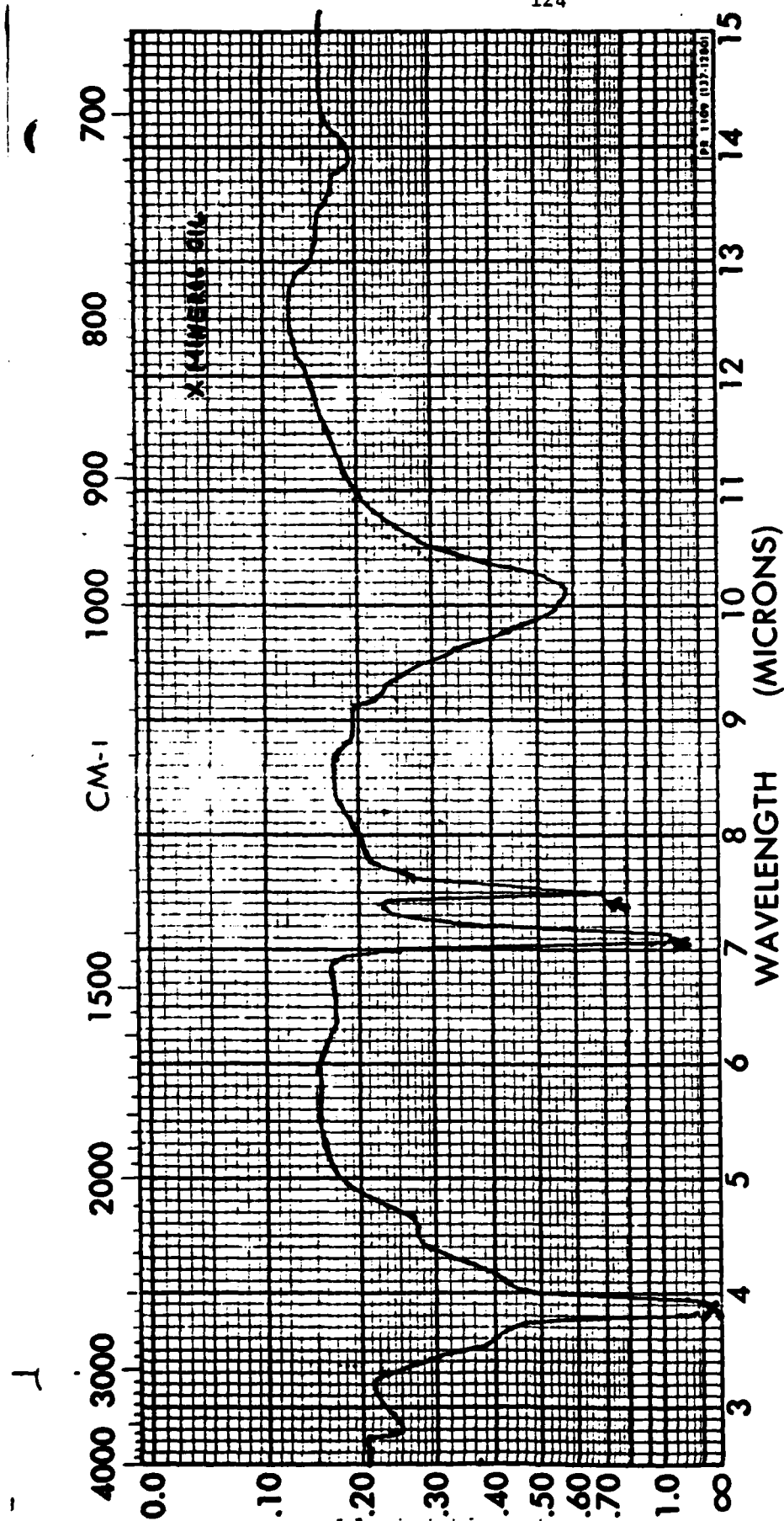


Fig. 81 - Infrared absorption spectrum of SET-45 hot weather paste of high water content at 7 days.

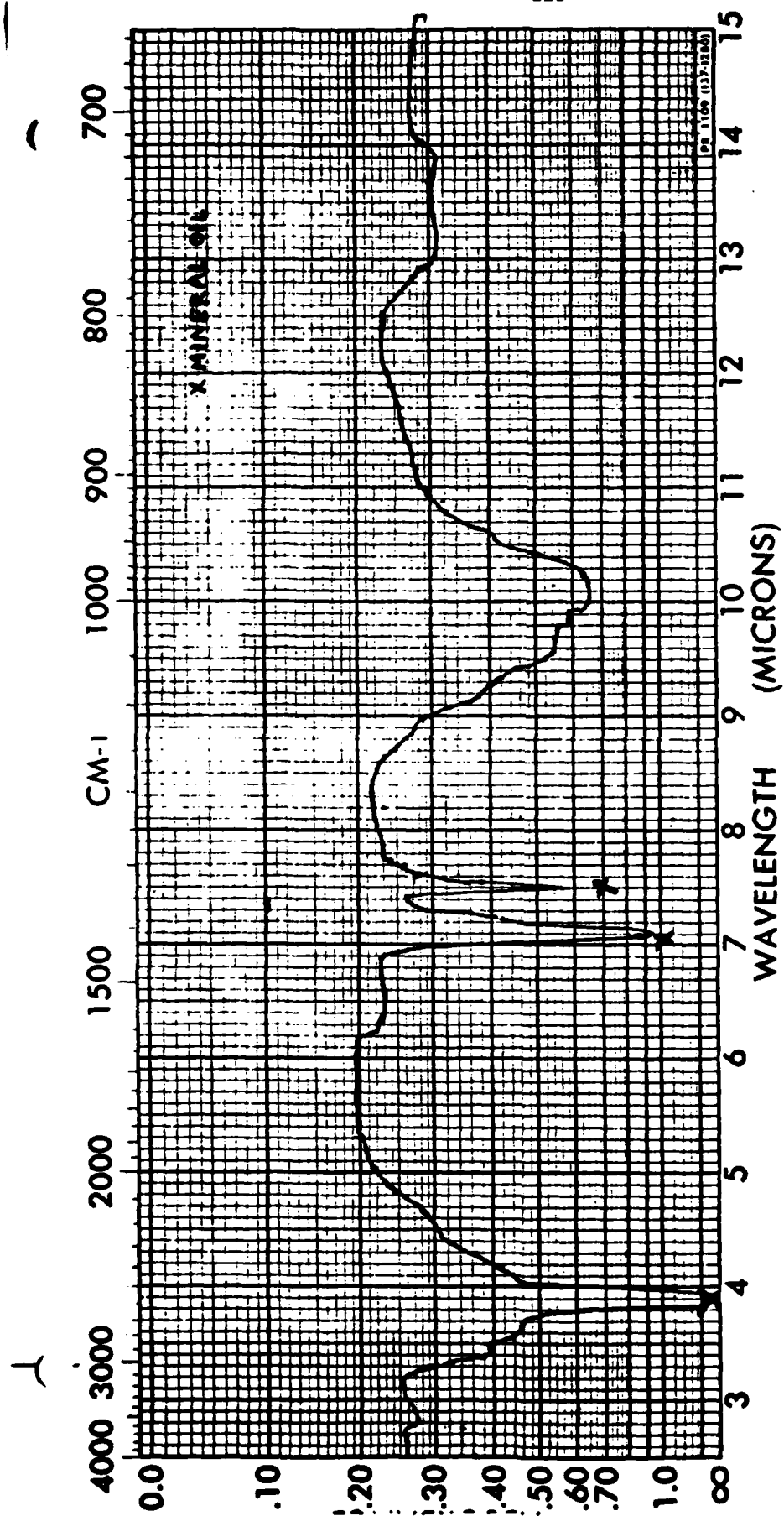


Fig. 82 - Infrared absorption spectrum of SET-45 cold weather paste of high water content at 7 days.

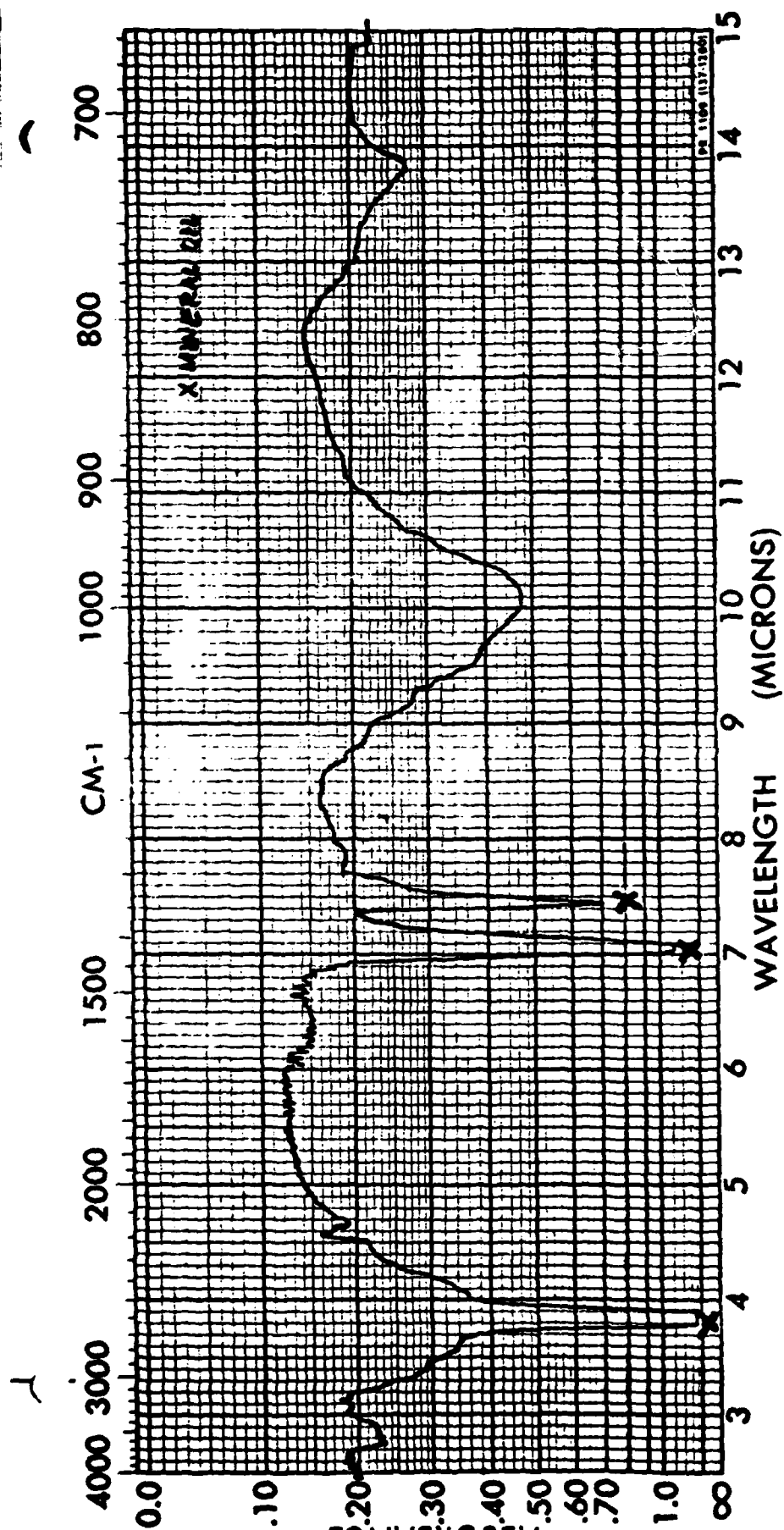


Fig. 83 - Infrared absorption spectrum of SET-45 cold:hot = 1:1 paste of high water content at 7 days.

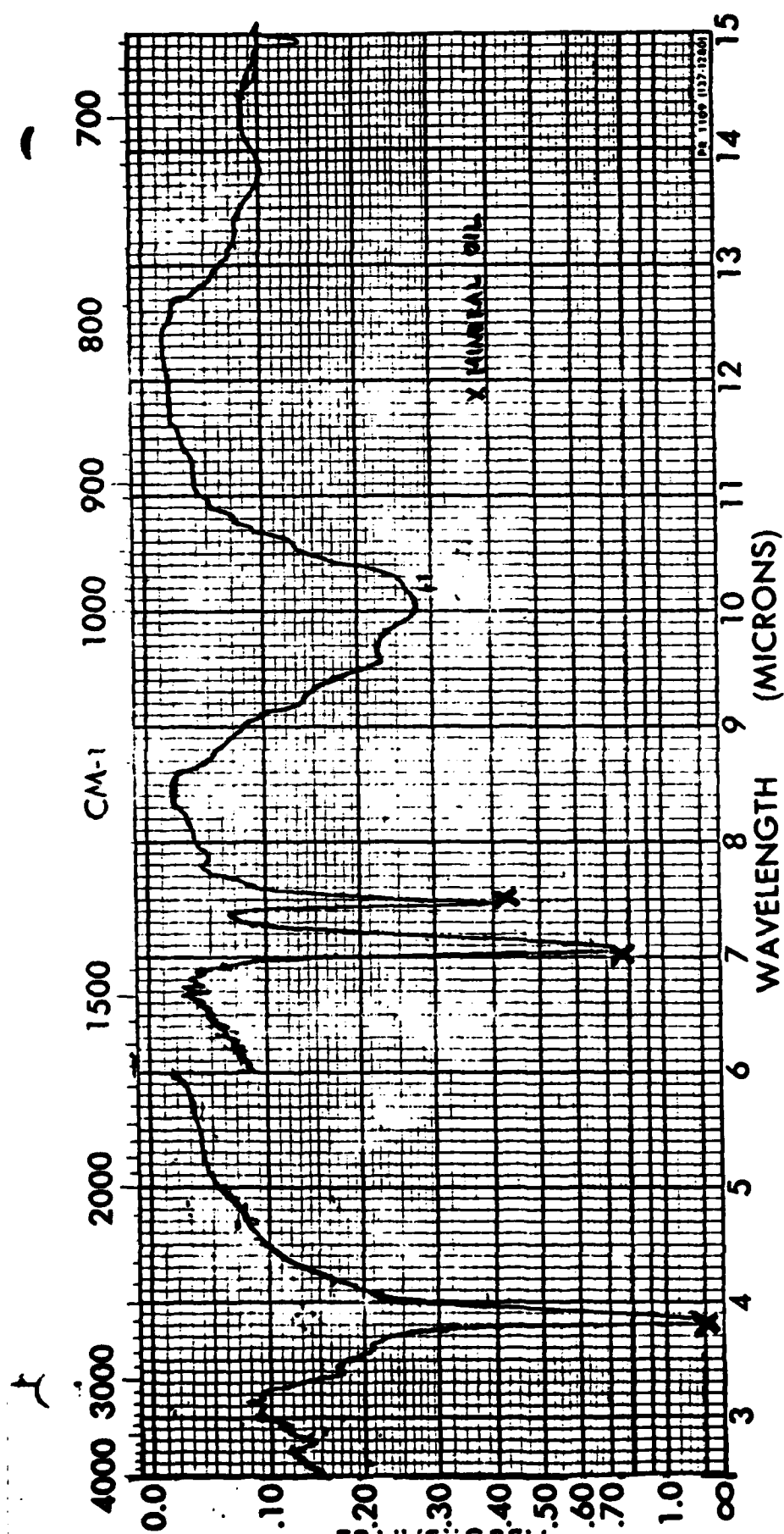


Fig. 84 - Infrared absorption spectrum of SET-45 cold weather paste of high water content with 1.7% borax at 7 days.

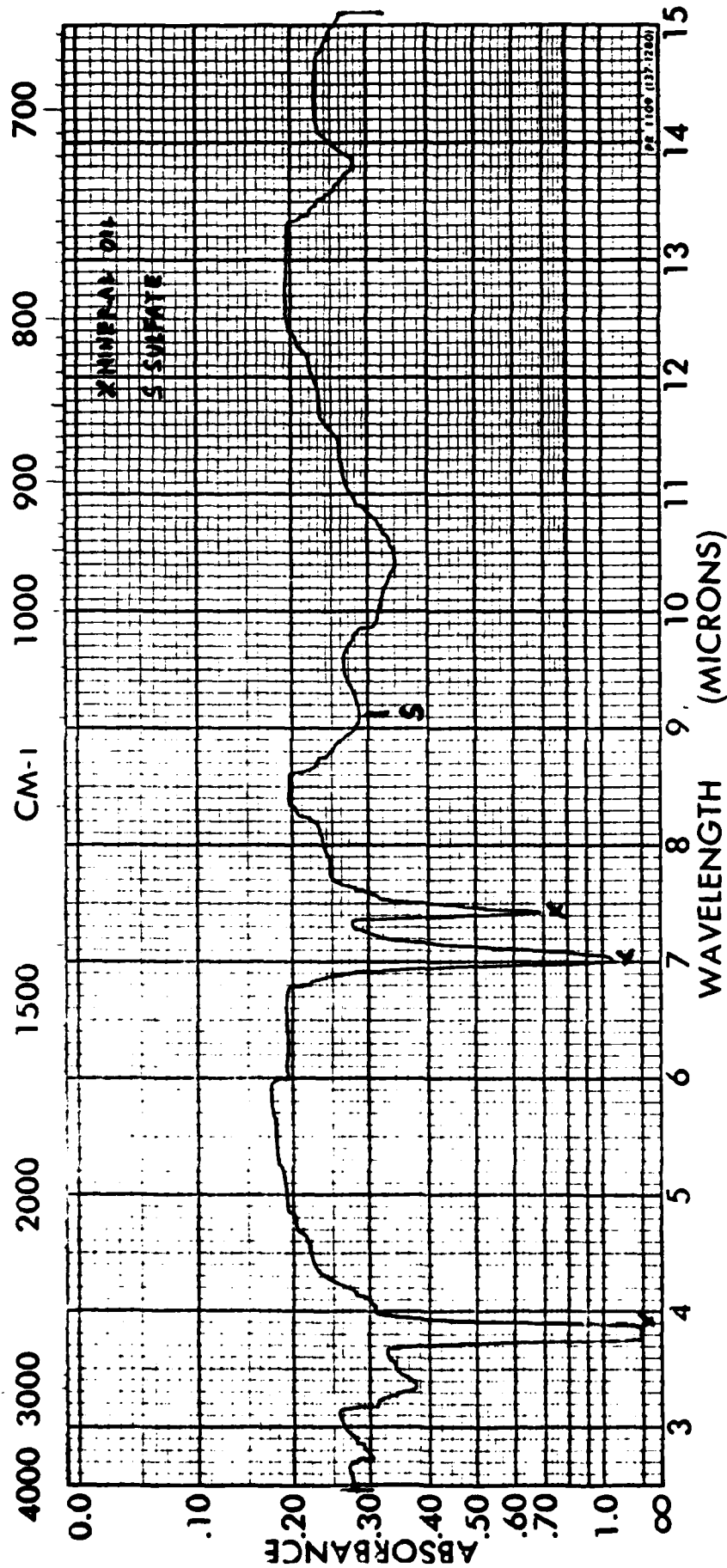


Fig. 85 - Infrared absorption spectrum of portland cement Type III paste of water-cement ratio 0.35 at 7 days.